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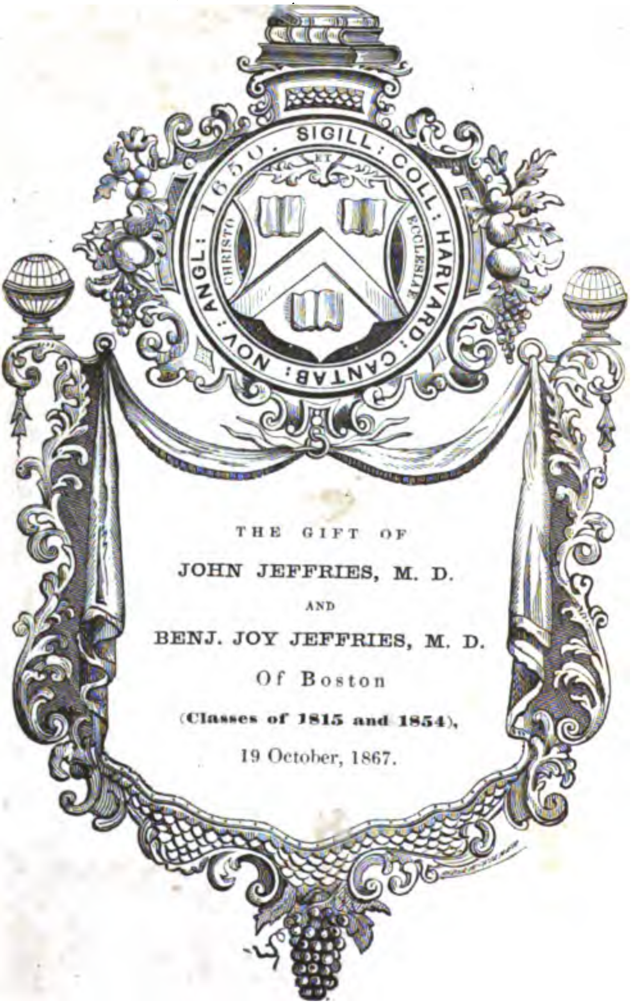
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19 October, 1867.

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ELEMENTS

OF

CHEMISTRY,

INCLUDING THE

RECENT DISCOVERIES AND DOCTRINES OF THE SCIENCE.

BY

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Edinburgh; and Member, and formerly President, of the
Royal Medical Society of Edinburgh.

FIFTH AMERICAN, FROM THE FIFTH LONDON EDITION.

WITH NOTES AND EMENDATIONS,

BY FRANKLIN BACHE, M.D.

PROFESSOR OF CHEMISTRY IN THE PHILADELPHIA COLLEGE OF PHARMACY; ONE OF
THE SECRETARIES OF THE AMERICAN PHILOSOPHICAL SOCIETY, &c.

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TO

FREDERICK STROMEYER, M.D. F.R.S. L. & E.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GÖTTINGEN,
ETC. ETC.

My dear sir,

The feelings of respect and regard which prompted me to dedicate to you the former editions of this Treatise, continue unaltered. Increasing experience, indeed, has served but to enhance the value which I ever attached to the instruction received in your laboratory, and to the habits of accuracy in research inculcated by your precept, and enforced by your example. To you, therefore, permit me still to inscribe a work intended to promote the study of that Science which you cultivate with so much zeal and success; and be assured that the opportunity of again publicly expressing gratitude for your kindness, and admiration of your distinguished analytical attainments, is a source of much pride and pleasure to your Friend and former Pupil,

EDWARD TURNER.

Nov. 1, 1834.

PREFACE

TO

THE FIFTH EDITION.

In preparing a fifth edition of these Elements, I have not lost sight of the plan on which the Work was originally framed. Its object is still, without entering minutely into the details of processes and experiments, to present a concise and connected view of the facts and theories of Chemistry. It has been found impossible, so numerous are the cultivators of this science, and so rapid its progress, to avoid numerous changes and additions. These have necessarily been interwoven with the texture of the volume, and it would be useless, were it practicable, to enter into an exact enumeration of them; but it may be convenient to some readers that the more important variations from former editions should be specified.

In the first section there are but few changes, and those relate chiefly to Radiant Heat. In that on Light, a summary of the laws of reflection and refraction, agreeably to the wishes of some of my pupils, has been supplied. The article on Electricity has been almost entirely recomposed; and, owing to the kindness of Mr. Snow Harris, I have been enabled to embody many results of his late researches, prior to their appearance in a printed form before the public. I have to acknowledge a similar kindness in Mr. Faraday, whose discoveries in Galvanism have compelled me to remodel the whole of the fourth section. To procure all the facts required for that purpose, I have been obliged to delay writing the section on Galvanism until the other parts of the volume were completed. This will account for the labours of Mr. Faraday not being referred to in other portions of the volume, which, though placed after the fourth section, were, in fact, printed some weeks earlier.

A few changes have been made in the section on the Laws of Combination, where will also be found a description of the mode of employing symbols in Chemistry. I ventured in the last edition to introduce chemical symbols as an organ of instruction, and subsequent experience has afforded such convincing evidence of their value in this point of view, that I cannot too earnestly urge the chemical student to employ them at an early period of his studies. The present state of Chemistry renders the use of abbreviated or symbolic language almost unavoidable; and the question now is, not so much whether they shall be used, as whether they shall be generally understood. To ensure this, it is essential that a uniform system be adopted; and I have hence felt the necessity of strictly conforming to the method introduced by Berzelius and adopted on the Continent. The tables which have been given in the sections of the second and third parts, with the primary view of showing analogies of chemical constitution, will serve the useful secondary purpose of supplying a guide to the employment of symbols. By reference to them, the student will see the meaning of any symbols he may meet with in the text.

The large number of compounds which have gradually accumulated, possessing the aspect and general characters of salts, and yet not composed of acids and alkalies in the general acceptation of these terms, have been arranged as separate orders of a large class of saline substances, which are inseparably allied by analogy of composition. But in associating substances naturally connected, I have abstained from violating any established usages in terminology. Changes in chemical nomenclature should be attempted rather by a community of chemists than by an individual; and if the labours of the Committee which the British Association has appointed for promoting uniformity in the use of symbols, shall be attended with that success which its proposer anticipates, a like task in reference to chemical nomenclature may well be imposed on the same Committee. For the greater part of our knowledge of the compounds here referred to, we are indebted to Berzelius, and the principal facts concerning them are drawn from his writings.

Owing to the activity displayed in organic analysis by several Continental chemists, especially by Liebig and Dumas, the necessary additions and changes in the Third Part have been very considerable. I am conscious that the arrangement of organic substances stands in need of revision; but it is easy to trace defects in any given arrangement on such a subject, and very difficult to fix on one which shall not be liable to equal objection. Considering facility of consultation of far more importance to the reader than critical propriety of classification, I have thought it right for the present to describe organic compounds nearly in the same order as in former editions.

In the Appendix will be found an interesting communication, kindly sent me by Mr. Graham, on the nature of certain hydrated salts and peroxides, and on phosphuretted hydrogen. It likewise contains other notices which either reached me too late for insertion in the body of the work, or were accidentally omitted.

I have again to express my thanks to Dr. Franklin Bache, Editor of the American edition, for several valuable suggestions.

LONDON, Nov. 1, 1834.

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OF

THE AMERICAN EDITOR.

In superintending a new impression of Dr. Turner's Elements from the fifth London edition, the American Editor has restricted himself, as on former occasions, to the duty of revising the text and supplying a few notes. His task, however, has been much increased, in consequence of the large number and peculiar nature of the additions made by the author. In these, numerous errors have been detected, especially in the Chemical tables, the inaccuracy of which has probably arisen from the difficulty of printing correctly a series of numbers from manuscript. From the pains which have been taken in revising the press, it is believed that the American edition will be found much more correct than the London work; while its convenient size will enable it to maintain its place, as the most popular manual of Chemistry that has yet been published in this country.

Philadelphia, Oct. 1835.

CONTENTS.

Page
Introduction 1

PART I.

IMPONDERABLE SUBSTANCES.

Sect. I. Heat, or caloric 5
  Communication of Heat by Contact 6
  Conduction of Heat 6
  Radiation 8
  Cooling of Bodies 14
  Effects of Heat 15
    Expansion 15
    Liquefaction 36
    Vaporization 41
  Constitution of Gases with respect to Heat 53
  Sources of Heat 54
II. Light 59
  Reflection of Light 55
  Refraction of Light 58
  Decomposition of Light 65
  Terrestrial Light 68
III. Electricity 71
  Theories of Electricity 73
  Causes of Electric Excitement 75
  Electroscopes and Electrometers 80
  Laws of Electrical Accumulation 83
  Historical Notice 86
IV. Galvanism 87
  Voltaic Arrangements or Circles 88
  Theories of Galvanism 94
  Laws of the Action of Voltaic Circles 97
  Effects of Galvanism 99
    Chemical Action of Galvanism 101
    Theory of Electro-chemical Decomposition 106
    Magnetic Effects of Galvanism 109
    Volta-electric Induction 117

PART II.

Inorganic Chemistry.

Preliminary Remarks 121

Sect. I. Affinity 124
  Changes that accompany Chemical Action 127

Page
Circumstances that modify and influence the operation of Affinity 128
Measure of Affinity 133
Sect. II. Proportions in which Bodies unite, and the Laws of Combination 134
Chemical Equivalents of Elementary Substances 141
Atomic Theory 142
Theory of Volumes 144
Chemical Symbols 150
Isomeric Bodies 152
III. Oxygen 153
Theory of Combustion 156
IV. Hydrogen 158
Water 161
Peroxide of Hydrogen 163
V. Nitrogen 166
The Atmosphere 167
Protoxide of Nitrogen 174
Binoxide of Nitrogen 176
Hyponitrous Acid 178
Nitrous Acid 179
Nitric Acid 181
VI. Carbon 184
Carbonic Acid 187
Carbonic Oxide Gas 189
VII. Sulphur 191
Sulphurous Acid Gas 192
Sulphuric Acid 194
Hyposulphurous Acid 196
Hyposulphuric Acid 197
VIII. Phosphorus 198
Oxide of Phosphorus 200
Hypophosphorous Acid 201
Phosphorous Acid 201
Phosphoric Acid 202
Pyrophosphoric Acid 203
Metaphosphoric Acid 204
IX. Boron 204
Boracic Acid 204
X. Selenium 206
Oxide of Selenium 207
Selenious Acid 207
Selenic Acid 207
XI. Chlorine 209
Hydrochloric Acid 212
Protoxide of Chlorine 216
Peroxide of Chlorine 217
Chlorous Acid 217
Chloric Acid 217
Perchloric Acid 218
Quadrochloride of Nitrogen 219
Chlorides of Carbon 219
Dichloride of Sulphur 221
Chlorides of Phosphorus 221
Chlorocarbonic Acid Gas 222
Chloral 222
Terchloride of Boron 223
Chloro-nitrous Gas 223

Page
Nature of Chlorine 224
SECT. XII. Iodine 226
Hydriodic Acid 228
Oxide of Iodine and Iodous Acid . . . 229
Iodic Acid 229
Periodic Acid 230
Chlorides of Iodine 231
Teriodide of Nitrogen 231
Iodides of Phosphorus 232
Iodide of Sulphur 232
Periodide of Carbon 232
XIII. Bromine 233
Hydrobromic Acid 235
Bromic Acid 236
Chloride of Bromine 237
Bromide of Iodine 237
Bromide of Sulphur 237
Bromides of Phosphorus 237
Bromide of Carbon 238
XIV. Fluorine 238
Hydrofluoric Acid 238
Fluoboric Acid 240

COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER 242

SECT. I. Hydrogen and Nitrogen.—Ammoniacal Gas . . 242
II. Compounds of Hydrogen and Carbon . . . 244
Light Carburetted Hydrogen 245
Olefiant Gas 247
Etherine 250
Bicarburet of Hydrogen 251
Paraffine 251
Eupione 252
Naphtha 252
Naphthaline 253
Paranaphthaline 255
Idrialine 255
Camphene 255
Citrene 256
Coal and Oil Gas 256
III. Compounds of Hydrogen and Sulphur . . . 258
Hydrosulphuric Acid 258
Persulphuret of Hydrogen 260
IV. Hydrogen and Selenium.—Hydroselenic Acid . . 261
V. Compounds of Hydrogen and Phosphorus . . . 262
Phosphuretted Hydrogen 262
Perphosphuretted Hydrogen 263
VI. Compounds of Nitrogen and Carbon 264
Bicarburet of Nitrogen or Cyanogen Gas . . 264
Hydrocyanic or Prussic Acid 266
Cyanic Acid 270
Fulminic Acid 272
Cyanuric Acid 273
Chloride of Cyanogen 274
Bichloride of Cyanogen 275
Iodide of Cyanogen 275
Bromide of Cyanogen 276
Hydrosulphocyanic Acid 276

Page
Bisulphuret of Cyanogen . . 277
Cyano-hydrosulphuric Acid . . 277
Sulphuret of Cyanogen . . 277
Hydroseleniocyanic Acid . . 278
SECT. VII. Compounds of Sulphur with Carbon, &c. . 278
Bisulphuret of Carbon . . . 278
Sulphuret of Phosphorus . . 279
Bisulphuret of Selenium . . . 279
Seleniuret of Phosphorus . . 279

GENERAL PROPERTIES OF METALS 279
SECT. I. Potassium 294
Protoxide (Potassa) 296
Peroxide 298
Chloride and Iodide 298
Bromide and Fluoride . . . 299
Hydurets and Carburet . . . 299
Sulphurets 299
Phosphurets and Seleniurets . . 300
Cyanurets 300
Sulphocyanuret 301
II. Sodium 301
Protoxide (Soda) 302
Peroxide 302
Chloride 302
Iodide, Bromide, and Fluoride . . 303
Sulphuret 303
Chloride of Soda 303
III. Lithium. 305
Protoxide (Lithia) 305
Chloride and Fluoride 306
IV. Barium 306
Protoxide (Baryta) 307
Peroxide 307
Chloride, Iodide, Bromide, and Fluoride 308
Sulphuret 308
Cyanuret and Sulphocyanuret . . 309
V. Strontium 309
Protoxide (Strontia) 309
Peroxide 310
Chloride, Iodide, and Fluoride . . 310
Protosulphuret 310
VI. Calcium 310
Protoxide (Lime) 311
Peroxide 312
Chloride, Iodide, Bromide, and Fluoride . 312
Sulphurets 313
Phosphuret 313
Chloride of Lime 313
VII. Magnesium 314
Protoxide (Magnesia) 314
Chloride, Iodide, Bromide, and Fluoride 315
VIII. Aluminium 315
Sesquioxide (Alumina) 317
Sesquichloride 318
Sesquisulphuret, Sesquiphosphuret, and Sesquiseleniuret 319
IX. Glucinium, Yttrium, Thorium, and Zirconium 319

Page
Glucinium 319
Yttrium 320
Thorium 321
Zirconium 322
Sect. X. Silicium 323
Silicic Acid (Silica) . . . 324
Chloride 325
Bromide and Sulphuret . . 326
Fluosilicic Acid 326
XI. Manganese 327
Sesquioxide 328
Peroxide and Protoxide . . . 329
Red Oxide and Varvicite . . . 331
Manganic and Permanganic Acid . 332
Chlorides and Perfluoride . . . 333
Protosulphuret 334
XII. Iron 334
Protoxide, Peroxide, and Black Oxide . 337
Chlorides and Iodides . . . 338
Bromides and Fluorides . . 339
Sulphurets 339
Phosphurets 340
Carburets 340
Protocyanuret and Sulphocyanurets . 341
XIII. Zinc and Cadmium 341
Zinc 341
Cadmium 343
XIV. Tin 345
Protoxide 345
Sesquioxide and Binoxide . . . 346
Chlorides 346
Iodides 347
Sulphurets 347
Terphosphuret 348
XV. Cobalt and Nickel 348
Cobalt 348
Nickel 350
XVI. Arsenic 353
Arsenious Acid 354
Arsenic Acid 357
Chlorides 357
Periodide 357
Sesquibromide 358
Protohyduret and Arseniuretted Hydrogen 358
Sulphurets 358
XVII. Chromium and Vanadium . . . 359
Chromium 359
Vanadium 363
XVIII. Molybdenum, Tungsten, and Columbium . 368
Molybdenum 368
Tungsten 371
Columbium 373
XIX. Antimony 374
Sesquioxide 375
Antimonious and Antimonic Acid . . 377
Chlorides 377
Bromide 378

Page
Sulphurets 378
Oxy-sulphuret 378
SECT. XX. Uranium and Cerium 379
Uranium 379
Cerium 381
XXI. Bismuth, Titanium, and Tellurium . . 382
Bismuth 382
Titanium 283
Tellurium 385
XXII. Copper 387
Red Oxide 387
Black Oxide and Superoxide . . 389
Chlorides 389
Iodides 390
Sulphurets and Phosphurets . . 390
Cyanuret and Disulphocyanuret . . 391
XXIII. Lead 391
Dinoxide and Protoxide . . . 392
Red Oxide and Peroxide . . 393
Chloride, Iodide, Bromide, and Fluoride 394
Sulphurets, Phosphuret, Carburet, and Cyanuret 394
XXIV. Mercury or Quicksilver . . . 395
Protoxide and Peroxide . . 396
Protochloride 396
Bichloride 397
Iodides 398
Bromides 399
Sulphurets 399
Bicyanuret 399
XXV. Silver 400
Oxide 401
Chloride, Iodide, Cyanuret, and Sulphuret 402
XXVI. Gold 402
Oxides 403
Chlorides 404
Tersulphuret 406
XXVII. Platinum 406
Oxides 407
Chlorides, Iodides, and Sulphurets . 408
XXVIII. Palladium, Rhodium, Osmium, and Iridium . 409
Palladium 409
Rhodium 410
Osmium 412
Iridium 413
XXIX. Metallic Combinations 414
Amalgams 416
Alloys 416

GENERAL REMARKS ON SALTS 419
Crystallization 424
SECT. I. Oxy-salts 433
Sulphates 434
Double Sulphates 441
Sulphites 443
Nitrates 444
Nitrites 448
Chlorates 448

Page
Iodates 449
Phosphates 450
Pyrophosphates 455
Metaphosphates 456
Arseniates 456
Arsenites 459
Chromates 459
Borates 460
Carbonates 461
SECT. II. Hydro-salts 467
Ammoniacal salts 468
Phosphuretted Hydrogen Salts . . . 470
III. Sulphur-salts 470
Hydro-sulphurets 471
Hydro-sulphocyanurets 472
Carbo-sulphurets 473
Arsenio-sulphurets 474
Molybdo-sulphurets 476
Antimonio-sulphurets 476
Tungsto-sulphurets 477
IV. Haloid Salts 477
Hydrargo-chlorides 478
Auro-chlorides 478
Platino-chlorides 479
Palladio-chlorides 480
Rhodio-chlorides 480
Iridio-chlorides 481
Osmio-chlorides 481
Oxy-chlorides 481
Chlorides with Ammonia . . . 482
Chlorides with Phosphuretted Hydrogen . 482
Double Iodides 483
Double Bromides and Fluorides . . 484
Boro-fluorides 484
Silico-fluorides 485
Titano-fluorides 486
Oxy-fluorides 486
Double Cyanurets.—Ferro-cyanurets . . 486
Ferro-sesquicyanurets 489
Zinco-cyanurets 492

PART III.

ORGANIC CHEMISTRY.

VEGETABLE CHEMISTRY 495
SECT. I. Vegetable Acids 497
Oxalic Acid 498
Acetic Acid 502
Lactic Acid 505
Kinic Acid 506
Malic Acid 507
Citric Acid 508
Tartaric Acid 509
Racemic Acid 511

Page
Benzoic Acid 512
Meconic Acid 513
Metameconic and Tannic Acid . . 514
Gallic Acid 516
Pyrogallic Acid 517
Metagallic, Ellagic, Succinic, and Mucic Acid 518
Camphoric, Valerianic, Rocellic, and Moroxylic Acid 519
Chloroxalic, Boletic, Igasuric, Suberic, Zumic, and Pectic Acid 520
Lactucic, Crameric, Caincic, and Indigotic Acid 521
Carbazotic Acid 522
SECT. II. Vegetable Alkalies 524
Morphia 524
Narcotina 526
Codeia 527
Narceia and Cinchonia . . . 528
Quinia 529
Aricina and Strychnia . . . 530
Brucia, Veratria, and Emetia . . 531
Picrotoxia, Corydalia, Solania, Cynopia, and Delphia 532
Sanguinaria and Nicotina 533
III. Neutral Substances 533
Sugar 534
Starch or Fecula.—Amidine . . . 536
Gum . - 537
Lignin 539
IV. Oleaginous, Resinous, and Bituminous Substances 539
Oleaginous Substances 540
Fixed Oils 540
Volatile or Essential Oils 541
Essence of Turpentine . . 542
Camphor 543
Oil of Cloves and Oil of Mustard . 543
Oil of Bitter Almonds . 543
Benzule 543
Benzamide 545
Benzoine 545
Coumarin 545
Resinous Substances 546
Resins 546
Amber, Balsams, Gum-resins, and Caoutchouc 547
Wax 548
Bituminous substances 549
Bitumen 549
Petroleum, Asphaltum, Mineral Pitch, and Retinasphaltum . . 549
Inflammable principles of Tar . 549
Creosote 549
Picamar and Capnomor . 550
Pittacal 551
Pit-coal 551
Brown Coal and Common or Black Coal 551
Glance Coal 552
V. Spirituous and Ethereal Substances . . 552
Alcohol 552

Page
Ether 554
Sulpho-vinic Acid 557
Ethero-sulphuric and Ethero-phosphoric Acid 558
Oil of Wine 559
Hydrochloric Ether 559
Hydriodic, Hydrobromic, Nitrous, and Oxalic Ether 560
Acetic, Cyanuric, Sulphocyanic, and Chloric Ether 561
Pyroacetic and Pyroxylic Spirit . 562
SECT. VI. Colouring Matters 563
Blue Dyes 564
Red Dyes 566
Yellow Dyes 567
Black Dyes 567
VII. Substances which, so far as is known, do not belong to either of the preceding Sections . 568
Vegetable Albumen and Gluten . . 568
Yeast and Asparagin 569
Bassorin and Caffein 570
Cathartin, Fungin, Suberin, Ulmin, Lupulin, &c. 571
Olivile, Sarcocoll, Rhubarbarin, Rhéin, Rhaponticin, &c. 572
Scillitin, Senegin, Saponin, Arthanatin, Extractive Matter, &c. 573
Salicin, Populin, and Meconin . . 574
Columbin, Elatin, and Sinapisin . . 575
VIII. Spontaneous Changes of Vegetable Matter . 576
Saccharine Fermentation . . . 576
Vinous Fermentation 577
Acetous Fermentation 579
Putrefactive Fermentation . . . 580
IX. Chemical Phenomena of Germination and Vegetation 581
Germination 581
Growth of Plants 583
Food of Plants 585

ANIMAL CHEMISTRY 587
PROXIMATE ANIMAL SUBSTANCES 587
SECT. I. Substances which are neither Acid nor Oleaginous 587
Fibrin 587
Albumen 588
Gelatin 590
Urea 591
Sugar of Milk and Sugar of Diabetes . 592
II. Animal Acids 593
Uric or Lithic Acid . . . 593
Purpuric and Rosacic Acid . . . 594
Hippuric and Formic Acid . . 595
Allantoic Acid 596
III. Animal Oils and Fats 596
Train Oil, Spermaceti Oil, Animal Oil of Dippel, &c. 597
Margarine, Oleine, and Margaric and Oleic Acid 598
Stearic and Sebacic Acid, Butyrine, Phocenine, Hircine, and Glycerine . . 599

Page
Spermaceti, Ethal, Adipocire, and Cholesterine 600
Ambergris, Ambreine, and Ambreic Acid 601

MORE COMPLEX ANIMAL SUBSTANCES, AND SOME FUNCTIONS OF ANIMAL BODIES 601

SECT. I. Blood, Respiration, and Animal Heat . . 601
Blood 601
Respiration 609
Animal Heat 615
II. Secreted Fluids Subservient to Digestion . 617
Saliva 617
Pancreatic and Gastric Juice . . 618
Bile 619
Biliary Concretions . . . 620
III. Chyle, Milk, and Eggs 621
Chyle 621
Milk 622
Eggs 624
IV. Liquids of Serous and Mucous Surfaces, &c. . 625
Humours of the Eye . . . 625
Mucus 625
Pus 626
Sweat 627
V. Urine and Urinary Concretions . . . 627
Urine 627
Urinary Concretions 631
VI. Solid Parts of Animals 633
Bones 633
Teeth, Horn, Tendons, Muscle, &c. . 634
VII. Putrefaction 635

PART IV.

ANALYTICAL CHEMISTRY.

SECT. I. Analysis of Mixed Gases 637
II. Analysis of Minerals 639
III. Analysis of Mineral Waters 644
Composition of Mineral Waters . . . 648

APPENDIX.

Constitution of certain Hydrated Salts and Peroxides, and of Phosphuretted Hydrogen . . 652
Table of the Force of Aqueous Vapour . 655
Table of the Force of the Vapours of Alcohol, Ether, &c. 657
Table of the Strength of Sulphuric Acid . 658
Table of the Strength of Nitric Acid . . 659
Table of the Strength of Alcohol . . 660
Table of Specific Gravities corresponding to the Degrees of Baumé's Hydrometer . . 661

Mercaptan and Mercaptum . . . 661
Mellon, Melam, Melamine, Ammeline, and Ammelide 662
Carburetted Hydrogen in the Atmosphere 663
Nituret of Phosphorus 663
Benzin and Benzone 663
Origin of Naphtha 664
Xanthic and Hydroxanthic Acid . . 664
INDEX 665

INTRODUCTION.

Material substances are endowed with two kinds of properties, physical and chemical; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, *Natural Philosophy* and *Chemistry*.

The physical properties are either general or secondary. The general are so called because they are common to all bodies; the secondary, from being observable in some substances only. Among the general may be enumerated extension, impenetrability, mobility, extreme divisibility, gravitation, porosity, and indestructibility.

Extension is the property of occupying a certain portion of space: a substance is said to be *extended* when it possesses length, breadth, and thickness. By *impenetrability* is meant that no two portions of matter can occupy the same space at the same moment. Everything that possesses extension and impenetrability is matter.

Matter, though susceptible of rest and motion, has no inherent power either of beginning to move when at rest, or of arresting its progress when in motion. Its indifference to either state has been expressed by the term *vis inertiæ*, as if it depended on some peculiar force resident in matter; but it arises, rather, from matter being absolutely passive, and thereby subject to the influence of every force which is capable of acting upon it.

Matter is divisible to an extreme degree of minuteness. A grain of gold may be so extended by hammering that it will cover 50 square inches of surface, and contain two millions of visible points; and the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. (Nicholson's Introduction to Natural Philosophy, vol. i.) A grain of iron, dissolved in nitro-muriatic acid, and mixed with 3137 pints of water, will be diffused through the whole mass: by means of the ferro-cyanuret of potassium, which strikes a uniform blue tint, some portion of iron may be detected in every part of the liquid. This experiment proves the grain of iron to have been divided into rather more than 24 millions of parts; and if the same quantity of iron were still further diluted, its diffusion through the whole liquid might be proved by concentrating any portion of it by evaporation, and detecting the metal by its appropriate tests.

A keen controversy existed at one time concerning the divisibility of matter; some philosophers affirming it to be infinitely divisible, while others maintained an opposite opinion. Owing to the imperfection of our senses the question cannot be determined by direct experiment; because matter certainly continues to be divisible long after it has ceased to be an object of sense. The decision, if effected at all, can only be accomplished indirectly, as an inference from other phenomena. In favour of the former view it was urged, on mathematical grounds, that a surface admits of division without limit; and that to whatever degree matter is divided, it may still be conceived, in possessing extension and surface, to be susceptible of still further division. Plausible, however, as this mode of reasoning may appear, the opposite opinion is daily becoming more general. It is now commonly believed that matter consists of ultimate particles or molecules, which may indeed be conceived to be divisible, but which by hypothesis are assumed to be infinitely hard and impenetrable, and on that account to be incapable of division. These ultimate particles have received the appellation of *atoms*, (from the privative α and τεμνειν to cut,) as expressive of their nature. The arguments adduced in support of this opinion are principally drawn from the phenomena of chemistry, and from the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered in their proper place; but I may observe, in order to show the nature of the argument, that the supposed existence of atoms accounts for numerous facts, which cannot be satisfactorily explained on any other principle.

All bodies descend in straight lines towards the centre of the earth, when left at liberty at a distance from its surface. The power which produces this effect is termed *gravity*, *attraction of gravitation*, or *terrestrial attraction;* and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its *weight*. Every particle of matter is equally affected by gravity; and, therefore, the weight of any body will be proportionate to the number of ponderable particles which it contains.

The minute particles of which bodies consist, are disposed in such a manner as to leave certain intervals or spaces between them, and this arrangement is called *porosity*. These interstices may sometimes be seen by the naked eye, and frequently by the aid of glasses; but were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all; for if their contact were so perfect as to leave no interstitial spaces, then would it be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield. When, therefore, a body expands, the distance between its particles is increased; and, conversely, when it contracts or diminishes in size, its particles approach each other.

By *indestructibility* is meant, that, according to the present laws of nature, matter never ceases to exist. This statement seems at first view contrary to fact. Water and volatile substances are dissipated by heat, and lost; coals and wood are consumed in the fire, and disappear. But in these and all similar phenomena not a particle of matter is annihilated. The apparent destruction is owing merely to a change of form or composition; for the same material particles, after having undergone any number of such changes, may still be proved to possess the characteristic properties of matter.

The *secondary* properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and others of a like nature. Several of these properties, especially those last specified, depend on the relative intensity of two opposite forces—cohesion and repulsion. It is inferred, from the divisibility of matter, that the substance of solids and liquids is made up of an infinity of minute particles adhering together so as to constitute larger masses; and that the mutual adhesion of these particles is owing to a power of reciprocal attraction. This force is called *cohesion*, *cohesive attraction*, or the *attraction of aggregation*, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, and acts at sensible and frequently at very great distances; while cohesion exerts its influence only at insensible and infinitely small distances. It enables similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the force required to separate a hard body, such as iron or marble, into smaller fragments; or by the weight which twine or metallic wire will support without breaking.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact; and such would be the result of its influence, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of heat, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are, therefore, subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity.* The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other with very slight friction. Fluids are of two kinds; elastic fluids or aëriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is chiefly determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being in them counterbalanced by cohesion.

Matter is subject to another kind of attraction different from those yet mentioned, termed *chemical attraction* or *affinity*. Like cohesion, it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions attached to each other by cohesion, and the parts so attached are called *integrant* particles; each of which, however minute, being as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from marble, and are united by chemical attraction. They are the *component* or *constituent* parts of marble. The integrant particles of a body are, therefore, aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and, therefore, do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and B, A will quit B and unite by preference with C. The union of two substances is called *combination;* and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case *decomposition* is said to be effected.

The operation of chemical attraction, as thus explained, lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances; an attempt may be made to discover the proportion in which they unite; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

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* It should be borne in mind, however, that the force which tends to bring the elementary molecules into closer proximity, is derived from an innate property of ponderable matter; while the force which tends to separate them is dependent on the operation of a distinct principle, caloric, whose particles, being self-repellent, force the ponderable particles apart. In order to explain why the caloric remains attached to the ponderable molecules, it is necessary to suppose that its particles, though self-repellent, have an attraction for ponderable matter. *Ed.*

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound, which may be resolved into two or more parts; and those as simple or elementary, which contain but one kind of ponderable matter. The number of the latter amounts only to fifty-four; and of these all the bodies in the earth, as far as our knowledge extends, are composed. The list, a few years ago, was somewhat different from what it is at present; for the acquisition of improved methods of analysis has enabled chemists to demonstrate that substances, which were once supposed to be simple, are in reality compound; and it is probable that a similar fate awaits some of those which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By the former method the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen; by synthesis they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory; but when they are conjoined—when we first resolve a particle of water into its elements, and then reproduce it by causing them to unite—the evidence is in the highest degree conclusive.

I have followed, in the composition of this treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. The first comprehends an account of the nature and properties of *Heat*, *Light*, and *Electricity*,—agents so diffusive and subtile, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our most delicate balances, and hence they have received the appellation of *Imponderables*. They cannot be confined and exhibited in a mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is, therefore, questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles, which are applied to material substances in general; and I shall, therefore, consider them as such in my subsequent remarks.

The second part comprises *Inorganic Chemistry*. It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. Elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most convenient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with each other, will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with each other. The last division of this part will comprise a history of the salts.

The third general division of the work is *Organic Chemistry*, a subject which will be conveniently discussed under two heads, the one comprehending the products of vegetable, the other of animal life.

The fourth part contains brief directions for the performance of *Analysis*.

ELEMENTS
OF
CHEMISTRY.

PART I.

IMPONDERABLE SUBSTANCES.

SECTION I.

HEAT, OR CALORIC.

The term *Heat*, in common language, has two meanings: in the one case, it implies the sensation experienced on touching a hot body; in the other, it expresses the cause of that sensation. When used in the latter sense, it is synonymous with the word *Caloric*, (from *Calor*, heat,) which is employed exclusively to signify the cause or agent by which all the effects of heat are produced.

Heat, on the supposition of its being material, is a subtile fluid, the particles of which repel each other, and are attracted by all other substances. It is imponderable: that is, it is so exceedingly light, that a body undergoes no appreciable change of weight, either by the addition or abstraction of heat. It is present in all bodies, and cannot be wholly separated from them. For if a substance, however cold, be transferred into an atmosphere which is still colder, a thermometer placed in the body will indicate the escape of heat. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is inferred from the tendency it has to penetrate their particles, and to be retained by them.

Heat may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, heat passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each stands at the same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an *equilibrium*, of temperature. If, for example, a number of substances of different temperature be enclosed in an apartment, in which there is no actual source of heat, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all of them. The varying sensations of heat and cold, which we experience, are owing to a like cause. On touching a hot body, heat passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, heat is communicated to it from the hand, and thus arises the sensation of cold.

As this transfer of heat is constantly going forward, it is important to determine by what means, and according to what laws, the equilibrium is established. Now, it is found that heat is communicated from a hot body to others which are colder in two ways, by *direct contact*, and by what is called *radiation*. By *direct contact*, when the hot body touches a cold one, so that the heat may pass directly from one into the other; as when a bar of iron is put into a fire, or the hand plunged into hot water. By *radiation*, when the heat leaps as it were from a hot to a cold body through an appreciable interval; as when a red-hot ball, suspended in the vacuum of an air-pump, distributes its heat to surrounding objects, or as when we are warmed by standing at some distance before a fire. In studying these phenomena we must regard both the loss of heat in the hot body, and the gain of heat in the cold one. The mode in which a hot body cools is, firstly, by giving off heat from its surface either by contact or radiation, or both conjointly; and, secondly, by the heat in its interior passing from particle to particle through its substance to its surface. The heating of a cold body is effected, firstly, by heat passing into its surface either by contact or radiation, or by both conjointly; and, secondly, by the heat at its surface passing from particle to particle through its interior portions. Hence, in tracing the laws which regulate the distribution of heat, we shall successively consider the communication of heat from one body to another by *contact*, its passage from particle to particle of the same substance or the *conduction* of heat, and its transfer from a sensible distance or *radiation*.

COMMUNICATION OF HEAT BY CONTACT.

The principal conditions which influence the communication of heat from one body to another by contact, are the degree of contiguity and the conducting power of the substances. The more perfect the approximation, the more rapid, *cæteris paribus*, is the transfer. The contact of two solids, or of a solid with a gas, is in general of a less perfect kind, and at fewer points, than that between a solid and a liquid; and hence, so far as *contact alone* is concerned, the transfer is more rapid in the latter case than in the former. It is still more rapid when liquids are mixed with each other, or gases with gases, owing to the intermixture of their particles. When bodies touch each other at their surfaces only, the question becomes one of conduction, the rapidity of transfer depending on the velocity with which heat passes through the substances in contact. Thus, if a hot mass of iron and another of marble, of equal size, form, and temperature, be plunged into equal quantities of cold water, the iron will cool faster than the marble, because heat passes more rapidly through the substance of the former than through that of the latter. Were two pieces of hot iron similarly plunged, one into mercury and the other into water, the piece in contact with mercury would cool most rapidly, because that metal is a better conductor than water. Were the experiment made by immersing the iron in mercury and the marble in water, the rapidity of cooling in the former would very much exceed that in the latter, from two causes;—both from heat passing more rapidly through iron than through marble, and from its being conveyed away more rapidly by mercury than by water. The same principle explains the unequal sensation caused by bodies of equal temperature. Thus the hand receives a more vivid impression of warmth by touching hot iron than from glass of the same temperature; because the quantity of heat which in a given time can be brought from the interior to the surface of the hot body, so as to pass into the skin, is much greater in iron than in glass. In like manner, cold iron feels colder than glass of the same temperature; because the former conveys away from the skin more heat in a given time than the glass.

CONDUCTION OF HEAT.

By this term is expressed the passage of heat from particle to particle through the substance of bodies. Heat is said to be conducted by them, or to pass by *conduction*, and the property on which its transmission depends is termed *conducting power*.

Heat obviously passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. Daily experience teaches that though we cannot leave one end of a rod of iron for some time in the fire, and then touch its other extremity, without danger of being burned; yet this may be done with perfect safety with a rod of glass or of wood. The heat will speedily traverse the iron bar, so that, at the distance of a foot from the fire, it is impossible to support its heat; while we may hold a piece of red-hot glass two or three inches from its extremity, or keep a piece of burning charcoal in the hand, though the part in combustion be only a few lines removed from the skin. The observation of these and similar facts has led to the division of bodies into *conductors* and *non-conductors* of heat. The former division, of course, includes those bodies, such as the metals, which allow heat to pass freely through their substance; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood, and charcoal.

Various methods have been adopted for determining the relative conducting power of different substances. The mode devised by Ingenhouz* was to cover small rods of the same form, size, and length, but of different materials, with a layer of wax, to plunge their extremities into heated oil, and note to what distance the wax was melted on each during the same interval. The metals were found, by this method, to conduct heat better than any other substances; and of the metals, silver is the best conductor; gold comes next; then tin and copper, which are nearly equal; then platinum, iron, and lead.

Some experiments have lately been made by M. Despretz, apparently with great care, on the relative conducting power of the metals and some other substances, and the results are contained in the following table. (An. de Ch. et de Ph. xxxvi. 422.)

Gold	1000	Tin	303.9
Silver	973	Lead	179.6
Copper	898.2	Marble	23.6
Platinum	381	Porcelain	12.2
Iron	374.3	Fine clay	11.4
Zinc	363		

The substances employed for these experiments were made into prisms of the same form and size. To one extremity a constant source of heat was applied, and the passage of heat along the bar was estimated by small thermometers placed at regular distances, with their bulbs fixed in the substance of the prism.

An ingenious plan was adopted by Count Rumford (Phil. Trans. 1792,) for ascertaining the relative conducting power of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersion in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 135 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstices were filled with fine lint, it took place in 1032″; with cotton wool in 1046″; with sheep's wool in 1118″; with raw silk in 1284″; with beaver's fur in 1296″; with eider down in 1305″; and with hare's fur in 1315.″ The general practice of mankind is, therefore, fully justified by experiment. In winter we retain the animal heat as much as possible by covering the body with bad conductors, such as silk or woollen stuffs; and in summer cotton or linen articles are employed with an opposite intention.

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* Ingenhouz, Journal de Phys. 1789, p. 68.

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property. Count Rumford found a considerable difference in the conducting power even of the same material, according to the state in which it was employed. His observations seem to warrant the conclusion, that in the same substance the conducting power increases with the compactness of structure.

Liquids may be said, in one sense of the word, to have the power of conveying heat with great rapidity, though in reality they are very imperfect conductors. This peculiarity is owing to the joint influence of two circumstances,—the mobility which subsists among the particles of all fluids, and the change of size or volume invariably produced by a change of temperature. When any particles of a liquid are heated, they expand, thereby becoming specifically lighter than those which have not received an increase of temperature; and if the former happen to be covered by a stratum of the latter, these from their greater density will descend, while the warmer and lighter particles will be pressed upwards. It, therefore, follows that if heat enter at the bottom of a vessel containing a liquid, a double set of currents must be immediately established, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. Now these currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the fire being applied below, the upper one will begin to rise almost as soon as the lower. Hence, under certain circumstances, heat is communicated or rather *carried* through liquids with rapidity.

But if, instead of heating the bottom of the jar, the heat enter by the upper surface, very different phenomena will be observed. The intestine movements cannot then be formed, because the heated particles, from being lighter than those below them, remain constantly at the top; the heat can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water can conduct at all. In this, however, he was mistaken; for the opposite opinion has been successfully supported by Dr. Hope, Dr. Thomson, and the late Dr. Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting heat in a very slight degree.

It is extremely difficult to estimate the conducting power of aëriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by heat, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, these bodies allow a passage through them by radiation. Now the quantity of heat which passes by these two channels is so much greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

RADIATION.

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the heat being conveyed by means of a hot current; since all the heated particles have a uniform tendency to rise. Neither, for reasons above assigned, can it depend upon the conducting power of the air; because aërial substances possess that power in a very low degree, while the sensation in the present case is excited almost on the instant. There is yet another mode by which heat passes from one body to another; and as it takes place in all gases, and even *in vacuo*, it is inferred that the presence of a medium is not necessary to its passage. This mode of distribution is called *Radiation* of Heat, and the heat so distributed is called *Radiant*, or *Radiated Heat*. It appears, therefore, that a heated body suspended in the air cools, or is reduced to an equilibrium with surrounding bodies, in three ways; first, by the conducting power of the air, the influence of which is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Laws of Distribution. Heat is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the circumference of a circle; so that a thermometer placed at the same distance on any side would stand at the same point, if the effect of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without being arrested by the latter or in any way affecting its temperature. When they fall upon the surface of a solid or liquid substance, they may be disposed of in three different ways:—1, they may rebound from its surface, or be *reflected;* 2, they may be received into its substance, or be *absorbed;* and, 3, they may pass directly through it, or be *transmitted.* In the first and third cases, the temperature of the body on which the rays fall is altogether unaffected; whereas, in the second, it is increased. The heating influence varies with the distance from the radiating body. Common observation teaches that the heat of a fire is less, the further we are removed from it; just as the light grows faint in proportion as we recede from a lamp. The rate or law of decrease, as ascertained by careful experiment, and as may be inferred from mathematical considerations, is, that the intensity of heat diminishes in the same ratio as the squares of the distances from the radiating point increase. Thus the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The radiation of heat by hot bodies is singularly influenced by the nature and condition of their surfaces, a circumstance which was first examined by the late Sir John Leslie, to whose Essay on Heat, published in 1804, we must still refer for most of our knowledge on this subject. Leslie employed in his experiments a hollow tin cube filled with hot water as the radiating substance. The rays proceeding from it were brought, by means of a concave mirror, into a focus, in which the bulb of a differential thermometer was placed. By adapting thin plates of different metals to the sides of the tin cube, and turning them successively towards the mirror, he found a very variable effect produced upon the thermometer. A bright smooth polished plate of metal radiated very imperfectly; but if its surface were in the least degree dull or rough, the radiating power was immediately augmented. Or if the metallic surface were covered with a thin layer of isinglass, paper, wax, or resin, its power of radiation increased surprisingly. It follows from these researches that velocity of radiation depends more on the *surface* than the *substance* of a radiating body:—that the most imperfect radiators are to be sought among those bodies which are highly smooth and bright, such as polished gold, silver, tin, and brass; but that these same metals radiate freely when their smoothness and polish are destroyed, as by scratching their surfaces with a file, or covering them with whiting or lampblack. A metallic surface seems adverse to radiation independently of its smoothness, since a highly polished piece of glass radiates far better than an equally polished metallic surface. Scratching a surface probably favours radiation by multiplying the number of radiating points.

Some interesting experiments by Dr. Stark of Edinburgh have just appeared (Phil. Trans. 1833, Part II.) illustrative of the connexion between radiation and the colour of surfaces. The bulb of a delicate thermometer was successively surrounded by equal weights of differently coloured wool, was placed in a glass tube, heated by immersion in hot water to 180°, and then cooled to 50° in cold water. The times of cooling were 21 minutes with black wool, 26 with red wool, and 27 with white wool. Concurring results were obtained with flour of different colours. Likewise, black wool was found to collect more dew than an equal weight of white wool, other circumstances being alike. This is the first time that direct experiments, seemingly unexceptionable, have been made in proof of the influence of colour over radiation.

Reflection of Heat.—The existence of a reflecting power may be shown by standing at the side of a fire in such a position that the heat cannot reach the face directly, and then placing a plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire: as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from a radiating substance to the point of a plane surface by which its rays are reflected, and a second line from that point to the spot where its heating power is exerted, the angles which these lines form with a line perpendicular to the reflecting plane are called the angles of *incidence* and *reflection*, and are invariably equal to each other. It follows from this law, that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and that when these parallel rays impinge upon a second concave reflector standing opposite to the former, they are made to converge, so as to meet together in its focus. Their united influence is thus brought to bear upon a single point.

It has been known for ages that the heat contained in the solar rays admits of being reflected by mirrors, and a like property has long since been recognized in the rays emitted by red-hot bodies; but that heat emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light, is a modern discovery, noticed indeed by Lambert, but first decisively established by Saussure and Pictet of Geneva. They first proved it of an iron ball heated so as not to be luminous even in the dark, and then of a vessel of boiling water, (Pictet's Essai sur le Feu, p. 65, 1790); but for most of our knowledge of this subject we must again refer to the labours of Leslie. He demonstrated that the reflecting power depends on the nature and condition of surfaces, and that those qualities which are adverse to radiation, are precisely such as promote reflection. Bright smooth metallic surfaces, as polished silver, brass, or tin, which are retentive of their own heat, are little prone to receive heat from other sources, but cause such rays to fly off from them; while those qualities of a surface which facilitate radiation from a hot body, likewise unfit it for reflecting the rays which fall upon it from surrounding objects. His experiments, indeed, justify the conclusion that the faculty of radiation is inversely as that of reflection.

Absorption of Heat.—Every increase of temperature arising from radiant heat is due to its absorption or reception into the body on which it falls. It is admitted that heat cannot be transmitted directly through opaque bodies, and; therefore, that all the rays impinging on such objects must either be reflected or absorbed: those which are reflected, cannot be absorbed; and those which are not reflected, must be absorbed. The number of absorbed rays is supplemental to that of the reflected rays. It hence follows that as the reflecting power is materially influenced by the nature of surfaces, the absorptive power must be so likewise. Those qualities of a surface which increase reflection are to the same extent adverse to absorption; and those which favour absorption are proportionally injurious to reflection. Since, moreover, as was shown in the last article, the property of radiation is inversely as that of reflection, the power of radiating is directly proportional to that of absorbing heat.* These inferences are fully justified by the researches of Leslie, and have received additional confirmation by a decisive experiment made by my colleague, Dr. Ritchie. (Royal Inst. Journal, v. 305.)

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* The remarks of the author on the passage of caloric through surfaces, may, perhaps, be extended with advantage. Surfaces, as to the transmission of caloric, may be divided into two sets; 1st, those which offer an easy passage to caloric, either inwards or outwards; and 2d, those through which caloric passes with difficulty. The first set of surfaces are at the same time good absorbers and radiators; the second set combine the qualities of good

The colour of surfaces influences the absorption of radiant heat. This has been observed by several persons of the sun's rays, and of terrestrial heat associated with light, as will be stated in the next section; but the dependence of the absorptive power for simple heat on colour has not till lately been noticed. From researches by Dr. Stark already referred to (page 9), it seems that differently coloured wools wound upon the bulb of a thermometer, and exposed within a glass tube to hot water, rose from 50° to 170° in the following times,—black wool in 4' 30'', dark green in 5', scarlet in 5' 30'', white in 8'.

An interesting connexion has been traced by MM. Nobili and Melloni between the absorbing and conducting power of surfaces. (An. de Ch. et de Ph. xlviii. 198.) In their experiments, variations of temperature were estimated by a new instrument called *thermo-multiplier*, consisting of a thermo-electric combination on the principle of those to be hereafter described in the article on *Thermo-Electricity:* it is attached to a delicate galvanometer, which acts as a thermometer by measuring the degree of galvanic excitement, which excitement is thought to vary directly as the temperature. These researches, if free from fallacy, justify the inference that the radiating and absorbing powers of surfaces for simple heat are in the inverse order of their conducting power.

Transmission of Heat.—Radiant heat passes with perfect freedom through a vacuum. The air and gaseous substances present but a feeble barrier to its progress; so feeble, indeed, that the degree of impediment which they occasion has not yet been appreciated. Transparent media of a denser kind, on the contrary, such as the diamond, rock-crystal, glass, and water, even in thin strata, greatly interfere with its passage, and when in moderately thick masses intercept it altogether. This last remark, however, is only applicable to simple heat, that is, to heat unassociated with light. The solar rays pass readily through the substance of glass, both heat and light being refracted in their passage, as is shown by the operation of a burning-glass or lens; and though much of the heat emitted by the flame of a lamp, or a red-hot ball of iron, is arrested by glass, many calorific rays are directly transmitted along with the light. But the result is different when the heated body is not luminous. A thin screen of glass, interposed between such an object and a thermometer, certainly intercepts most of the rays that fall upon it; and the sole question which can be raised is, whether the small effect on the thermometer is caused by direct transmission, or by the screen first becoming warm by the absorption of the rays, and then acting on the thermometer by radiation. Leslie adopted the latter view, denying that any rays of simple heat can pass by direct transmission through glass; and Sir D. Brewster has supported this opinion by an argument suggested by his optical researches. (Phil. Trans. 1816, p. 106.) He discovered that when heat passes by conduction through the substance of glass, a crystalline arrangement of its particles is occasioned, the progress of which from particle to particle may be distinctly traced by the polarizing property which the crystalline points of the glass immediately assume. The same phenomena appear when radiant heat falls upon a plate of glass, and, therefore, it was inferred that the heat passes through by conduction and not by transmission. This argument, however, is scarcely conclusive; and I cannot help thinking that Mr. B. Powell, in his late very full digest of the whole subject of radiant heat (Reports of the British Association, p. 269) attaches to it more importance than it deserves. The observations of Sir D. Brewster afford undeniable evi-

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reflectors and retainers. The absorbing and radiating power on the one hand, and the reflecting and retaining power on the other, would, therefore, seem to be common properties, belonging to two distinct sets of surfaces. *Ed.*

dence of radiant heat being arrested by glass, a point which no one disputes; but it does not follow that *no* rays are transmitted. His method of inquiry was not calculated to detect transmitted rays, since they could not affect the temperature of the medium.

The most elaborate experiments in favour of the permeability of transparent media were conducted by De la Roche, who estimated the transmitted rays by the difference of effect occasioned by two glass screens, one of which was transparent and the other blackened. (Biot's Traité de Physique, iv. 638.) Prevost conducted a similar inquiry by employing moveable screens, which constantly presented a cool surface to the thermometer, thereby expecting to exclude all interference from conduction and secondary radiation; and some experiments on the same principle were performed some years ago by Dr. Christison and myself. Several ingenious experiments have been made on this subject by Dr. Ritchie; and it has lately been examined by MM. Nobili and Melloni with the aid of their thermo-multiplier. All these experimenters concur in the belief of direct transmission. The total effect from this cause is, however, very small; and with screens of moderate thickness it is wholly imperceptible. De la Roche found that the ratio of the transmitted to the intercepted rays continually augments, the nearer the temperature of the radiating body approaches to incandescence.

Theory of Radiation.—The tendency which all bodies evince to attain an equality of temperature by means of radiation, has given rise to two ingenious theories, suggested respectively by Pictet and Prevost. According to the former, bodies of equal temperature do not radiate at all; and when the temperature is unequal, the hotter give calorific rays to the colder bodies till an equilibrium is established, at which moment the radiation ceases. Prevost, on the contrary, conceived radiation to go on at all times, and from all substances, whether their temperature were the same or different from that of surrounding objects. (Recherches sur la Chaleur.) Consistently with this view, the temperature of a body falls whenever it radiates more heat than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it grows warm when the absorption exceeds the radiation. A hot body surrounded by others colder than itself, affords an instance of the first case; the second happens when all the substances within the sphere of each other's radiation have the same temperature; and the third occurs when a body is introduced into a room which is warmer than itself. Of these theories the preference is very generally accorded to the latter. Most of the phenomena of radiation, indeed, admit of a satisfactory explanation by both; but on the whole, the theory of Prevost is more generally applicable. A favourable example for tracing this preference is afforded by the law of cooling *in vacuo*, established by Dulong and Petit. Another argument in its favour is deducible from the close analogy which subsists between the laws of heat and light. Luminous bodies certainly exchange rays with one another. A feeble light sends rays to one of greater intensity; and the quantity of light emitted by each, does not seem to be at all influenced by the vicinity of the other. Since, therefore, the radiation of light is not prevented by the presence of other luminous bodies, it is probable that the radiation of heat is equally uninfluenced by the proximity of other radiating substances.

Adopting, for the reasons just stated, the theory of Prevost, it will be useful to examine a few instances of its application;—and, first, in regard to the experiments with conjugate mirrors. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, be of the same temperature as the surrounding objects (say at 60°), the thermometer will remain stationary. It will indeed receive rays from the ball; but as it emits an equal number in return, its temperature will be unchanged. If the ball is above 60° the thermometer will rise, because it then receives a greater number of rays than it gives out. If, on the contrary, the ball is below 60°, the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature will fall.

The same mode of reasoning explains an interesting experiment originally performed by the Florentine Academicians, and since carefully repeated by Pictet. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was withdrawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, endowed with the property of communicating coldness; whereas, all the preceding remarks were made on the supposition that cold is merely a negative quality arising from the diminution of heat. Nor is the foregoing experiment in the least degree inconsistent with such an opinion: on the contrary, it is readily accounted for by the theory of Prevost, and might have been anticipated by its application. The thermometer, in fact, has its temperature lowered, because it emits more rays than it receives; and it rises when the ice is removed, because it then receives a number of calorific rays radiated by the warmer surrounding objects, which were intercepted by the ice while it was in the focus.*

An elegant application of this theory was made by Dr. Wells to account for the formation of dew. The most copious deposite of dew takes place when the weather is clear and serene; and the substances that are covered with it are always colder than the contiguous strata of air, or than those bodies on which dew is not deposited. In fact, dew is a deposition of water previously existing in the air as vapour, and which loses its gaseous form only in consequence of being chilled by contact with colder bodies. In speculating, therefore, about the cause of this phenomenon, the chief object is to discover the cause of the reduction of temperature. The explanation proposed by Dr. Wells, in his excellent Treatise on Dew, and now almost universally adopted, is founded on the theory of Prevost. If it be admitted that bodies radiate at all times, their temperature can remain stationary only by their receiving from surrounding objects as many rays as they emit; and should a substance be so situated that its own radiation may continue uninterruptedly without an equivalent being returned to it, its temperature must necessarily fall. Such is believed to be the condition of the ground in a calm starlight evening. The calorific rays which are then emitted by substances on the surface of the earth, are dispersed through free space and lost: nothing is present in the atmosphere to exchange rays with them, and their temperature consequently diminishes. If, on the contrary, the weather be cloudy, the radiant heat proceeding from the earth is intercepted by the clouds, an interchange is established, and the ground retains nearly, if not quite, the same temperature as the adjacent portions of air.

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* In explaining the experiment of the apparent radiation of cold, it is necessary to distinguish two cases in which the equilibrium of temperature is disturbed; 1st, where a body is raised above the temperature of the surrounding medium; and 2d, where it is below the temperature of such medium. If a thermometer, after being heated to the boiling point, be held in the air, it immediately commences to project its caloric into the surrounding colder medium. If, however, we hold a ball of snow near the bulb of a thermometer which has been standing in a temperate apartment, the mercury falls, not because the caloric is projected from the instrument, but rather because the caloric is drawn into the snow. The calorific tension of the space occupied by the snow is diminished, and the caloric of the surrounding medium is drawn in by what might be conveniently called calorific induction. The effect, at first, is felt in the immediate vicinity of the cold body, and is thence propagated in right lines successively to greater and greater distances. If these views be admitted as correct, it will not be difficult to conceive how the direction of this motion of caloric by induction may be changed by the interposition of mirrors. There can be little doubt, that caloric constitutes a medium which pervades all space, and that rows of calorific particles in right lines must exist in every conceivable direction. In the experiment cited in the text, the ice in the focus of one mirror produces, by induction, a deficiency of caloric in its surface; a number of preexisting rays are drawn into the ice, which are continuous with an equal number parallel with the axis of the mirror. Let it be supposed that a particular row of particles is put in motion by induction, it is clear that a deficiency of caloric will be the consequence at some point on the surface of the mirror. This cannot be supplied by the mirror itself, and hence it will be made up by the first particle in the continuous parallel row. This produces an induction in the parallel row, which results in creating a deficiency of caloric in some point of the surface of the second mirror. Finally, a similar induction of caloric is created in the corresponding row of particles, leading to the focus of the second mirror where the thermometer is placed, which necessarily indicates a reduction of temperature. In this way we think the experiment of the radiation of cold may be explained, without the aid of M. Prevost's theory, which we conceive, on the whole, to be less simple than that of M. Pictet.—*Ed.*

All the facts hitherto observed concerning the formation of dew, tend to confirm this explanation. It is found that dew is deposited sparingly or not at all in cloudy weather; that all circumstances which promote free radiation are favourable to its deposition; that good radiators of heat, such as grass, wood, the leaves of plants, the filamentous substances in general, reduce their temperature, in favourable states of the weather, to an extent of ten, twelve, or even fifteen degrees below that of the circumambient air; and that while these are drenched with dew, pieces of polished metal, smooth stones, and other imperfect radiators, are barely moistened, and are nearly as warm as the air in their vicinity.

COOLING OF BODIES.

It appears from the preceding remarks on the transmission of heat, that the cooling of bodies takes place by two very different methods. When a hot body is enveloped in solid substances, its heat is withdrawn solely by means of communication, and the velocity of cooling is dependent on the conducting power. The refrigeration is effected in a similar manner when the heated body is immersed in a liquid; but the velocity of cooling depends partly on the conducting power of the liquid, and partly on the mobility of its particles. In elastic fluids the cooling takes place both by communication and radiation; and in a vacuum it is produced solely by radiation.

The term *velocity of cooling* above employed, signifies the number of degrees lost by a hot body during equal intervals of time, as one minute or one second; and by the *law of cooling* is meant the relation which the velocities of cooling bear to each other. The first attempt to fix the law of cooling was by Newton. Observing that the velocity of cooling in a hot body diminishes continually as the excess of its temperature declines, he conceived that the heat lost during each interval of time was a constant fraction of its excess of heat at the beginning of that interval. Thus, if a body, heated to 1000 degrees above the temperature of the surrounding air, were to lose 1-10th of that excess, or 100 degrees, during the first second, he thought it would lose 1-10th of the remaining 900, or 90 degrees, during the next second, and 1-10th of the residual 810, or 81 degrees, during the third second; so that the number of degrees lost during the first five seconds would be 100, 90, 81, 72·9, and 65·6. These numbers would, therefore, denote the velocity of cooling during each succeeding second; and on examining their mutual relation, it is obvious that they constitute a geometric progression, of which 1·111 is the ratio. For $65{\cdot}6 \times 1{\cdot}111 = 72{\cdot}9$, $65{\cdot}6 \times (1{\cdot}111)^2 = 80{\cdot}98$, $65{\cdot}6 \times (1{\cdot}111)^3 = 89{\cdot}96$, &c.;—the property of a geometrical series. As this view appeared to be consistent with actual observation, Newton inferred as a general law of cooling, that while the times of cooling form an arithmetical series, the velocities of cooling are in a geometric progression.

This subject has been experimentally investigated with remarkable ingenuity and success by Dulong and Petit. (An. of Phil. xiii, 112.) They have demonstrated that Newton's law of refrigeration may be adopted without material error when a body is but slightly hotter than the surrounding medium, and the whole decrease of its temperature is inconsiderable; but when the range of cooling is extensive, or the original excess of heat was great, the law is found to be very defective. They have examined, with consummate skill, the various circumstances by which the cooling of a hot body in a vacuum, and when surrounded by an elastic fluid, is influenced; but their inquiry is too mathematical and abstruse for the purposes of an elementary treatise.

EFFECTS OF HEAT.

The phenomena that may be ascribed to this agent, and which may, therefore, be enumerated as its effects, are numerous. With respect to animals, it is the cause of the feelings of cold, agreeable warmth, and burning, according to its intensity. It excites the system powerfully, and without a certain degree of it the vital actions would entirely cease. Over the vegetable world its influence is obvious to every eye. By its stimulus co-operating with air and moisture, the seed bursts its envelope and yields a new plant, the buds open, the leaves expand, and the fruit arrives at maturity. With the declining temperature of the seasons the circulation of the sap ceases, and the plant remains torpid till it is again excited by the stimulus of heat.

The dimensions of every kind of matter are regulated by this principle. Its increase, with few exceptions, separates the particles of bodies to a greater distance from each other, producing expansion, so that the same quantity of matter is thus made to occupy a larger space; and the diminution of heat has an opposite effect. Were the repulsion occasioned by this agent to cease entirely, the atoms of bodies would come into actual contact.

The form of bodies is dependent on heat. By its increase solids are converted into liquids, and liquids are dissipated in vapour; by its decrease vapours are condensed into liquids, and these become solid. If matter ceased to be under the influence of heat, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

When heat is accumulated to a certain extent in bodies, they shine or become *incandescent*. On this important property depend all our methods of artificial illumination.

Heat exerts a powerful influence over chemical phenomena. There is, indeed, scarcely any chemical action which is not in some degree modified by this principle; and hence a knowledge of its laws is indispensable to the chemist. By its means bodies previously separate are made to combine, and the elements of compounds are disunited. An undue proportion of it is destructive to all organic and many mineral compounds; and it is essentially concerned in combustion, a process so necessary to the wants and comforts of man.

Of the various effects of heat above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of its influence over the dimensions and form of bodies, a subject which will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

EXPANSION.

One of the most remarkable properties of heat is the repulsion which exists among its particles, a property which enables it, on entering into a body, to remove the integrant molecules of the substance to a greater distance from each other. The body, therefore, becomes less compact than befor occupies a greater space, or, in other words, expands. This effect of heat is opposed to cohesion—that force which tends to make the particles of matter approximate, and which must be overcome before any expansion can ensue. It may be expected, therefore, that a small addition of heat will occasion a small expansion, and a greater addition of heat a greater expansion; because in the latter case, the cohesion will be more overcome than in the former. It may be anticipated, also, that whenever heat passes out of a body, the cohesion being then left to act freely, a contraction will necessarily follow; so that expansion is only a transient effect, occasioned solely by the accumulation of heat. It follows, moreover, from this view, that heat should produce the greatest expansion in those bodies which are least influenced by cohesion, an inference fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in aëriform substances; while the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which will now be obvious, that all bodies are expanded by heat, and that the expansion of the same body increases with the quantity of heat which enters it. But this law does not apply, unless the form and chemical constitution of the body be preserved. For if a change in either be occasioned, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

In proof of the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness, of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. A familiar demonstration of the fact may be afforded by adapting a ring to an iron rod, the former being just large enough to permit the latter to pass through it while cold. The rod is next heated, and will then no longer pass through the ring. This dilatation from heat and consequent contraction in cooling takes place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, whose efforts have been chiefly directed towards ascertaining the exact quantity by which different substances are lengthened by a given increase of heat, and determining whether or not their expansion is equable at different temperatures. The Philosophical Transactions contain various dissertations on the subject by Ellicot, Smeaton, Troughton, and General Roy; and M. Biot, in his *Traité de Physique*, has given the results of experiments performed with great care by Lavoisier and Laplace. Their experiments establish the following points:—1. Different solids do not expand to the same degree from equal additions of heat. 2. A body which has been heated from the temperature of freezing to that of boiling water, and again allowed to cool to 32° F., recovers precisely the same volume which it possessed at first. 3. The dilatation of the more permanent or infusible solids is very uniform within certain limits; their expansion, for example, from the freezing point of water to 122°, is equal to what takes place betwixt 122° and 212°. The subsequent researches of Dulong and Petit, (An. de. C. et de P. vii.) prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond 212° the greater the expansion for equal additions of heat. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between 32° and 212°; but the differences which exist within this small range are so inconsiderable as to escape observation, and, therefore, for most practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace. (Biot, vol. i. p. 158.)

Names of Substances.	Elongation when heated from 32° to 212°.
Glass tube without lead, a mean of three specimens - -	$\frac{1}{1116}$ of its length.
English flint glass - -	$\frac{1}{1248}$
Copper - - -	$\frac{1}{581}$
Brass—mean of two specimens - -	$\frac{1}{532}$
Soft iron forged - - -	$\frac{1}{819}$
Iron wire - - - -	$\frac{1}{812}$
Untempered steel - -	$\frac{1}{927}$
Tempered steel - - -	$\frac{1}{807}$
Lead - - -	$\frac{1}{351}$
Tin of India - - -	$\frac{1}{516}$
Tin of Falmouth - -	$\frac{1}{462}$
Silver - - - -	$\frac{1}{524}$
Gold—mean of three specimens -	$\frac{1}{682}$
Platinum, determined by Borda - -	$\frac{1}{1167}$

Knowing the elongation of any substance for a given number of degrees of the thermometer, its total increase in bulk may in general be calculated by trebling the number which expresses its increase in length. Thus if a tube of flint glass elongates by $\frac{1}{1248}$, when heated from the freezing to the boiling point of water, its cubic space will have increased by $\frac{3}{1248}$ or $\frac{1}{416}$ of its former capacity. Strictly speaking this rule is not exact; but when the expansion of any substance, corresponding to the observed increase of temperature, is a minute fraction of its volume, the formula may be applied with safety. The error is then so small that it may be disregarded.*

The expansion of glass, iron, copper, and platinum, has been particularly investigated by M M. Dulong and Petit. The following table contains the result of their observations on glass. (An. de Ch. et de Ph. vii. 138.) It appears from the third column that at temperatures beyond 212°, glass expands in a greater ratio than mercury.

Temperature by an air thermometer.	Mean absolute dilatation of glass for each degree.	Temperature by a thermometer made of glass.
Fahr.	Fahr.	Fahr.
From 32° to 212°	$\frac{1}{69660}$	212°
—— 32 to 392	$\frac{1}{63540}$	415.8
—— 32 to 572	$\frac{1}{59220}$	667.2

The second, fourth, and sixth columns of the following table show the mean total expansion of iron, copper, and platinum, when heated from 32° to 212° and from 32° to 572°, for each degree. The third, fifth, and seventh columns indicate the degrees on a thermometer of iron, copper, and platinum, corresponding to a temperature of 572° on an air thermometer. It is obvious that platinum is much more uniform in its expansion than either of the other metals.

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* The reason of this is easily explained on geometric principles. Let 1 be the length of a cold metallic bar, and v its volume or solidity; let $1+d$ be its length when heated, and v' its volume in that state. As its breadth and thickness increase in the same proportion as its length, the expanded bar will have precisely the same figure, that is, the same proportion of its dimensions, as the cold one; and since, by Euclid, the solidity of similar figures is as the cube of homologous sides, it follows that $v : v' :: 1 : (1+d)^3$ or $1+3d+3d^2+d^3$. When, in solids, liquids, or gases, d happens to be a very small fraction, d^3 and even $3d^2$ are extremely minute, and may hence be altogether neglected.

Temp. by air thermometer.	Mean Dil. of iron in volume for each degree.	Temp. by iron rod thermometer.	Mean dilat. of copper in volume for each degree.	Temp. by copper rod thermometer.	Mean dilat. of platinum in volume for each degree.	Temp. by platinum rod thermometer.
Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.
212°	$\frac{1}{50760}$	212°	$\frac{1}{34920}$	212°	$\frac{1}{67860}$	212°
572°	$\frac{1}{40678}$	702.5	$\frac{1}{31860}$	623.8	$\frac{1}{65340}$	592.9

The expansion of liquids is readily proved by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation increases with the temperature; for if the thermometer be plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and, therefore, is enabled to contain more mercury than before; but the mercury being dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass, and is only the apparent, not the actual, expansion of the liquid.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. From the frequency with which the latter is employed in philosophical experiments, it is important to know the exact amount of its expansion. This subject has been investigated by several philosophers, but the experiments of Lavoisier and Laplace, and especially of Dulong and Petit, from the extreme care with which they were made, are entitled to the greatest confidence. According to the former, the actual dilatation of mercury, in passing from the freezing to the boiling point of water, amounts to $\frac{100}{5412}$ of its volume; but the result obtained by Dulong and Petit, who found it $\frac{100}{5550}$, is probably still nearer the truth. Adopting the last estimate, this metal dilates, for every degree of Fahrenheit's thermometer, $\frac{1}{9990}$ of the bulk which it occupied at the temperature of 32°. If the barometer, for instance, stand at 30 inches when the thermometer is at 32°, we may calculate what its elevation ought to be when the latter is at 60°, or at any other temperature.* The apparent expansion of mercury contained in glass is of course less than the absolute expansion. Between the limits of 32° and 212° F. Lavoisier and Laplace estimate the apparent expansion at $\frac{1}{63}$, and Dulong and Petit at $\frac{1}{64.8}$ of its volume, being $\frac{1}{11664}$ for each degree of Fahrenheit's thermometer. Dulong and Petit state, that the mean total expansion of mercury from 32° to 572° F. for each degree is $\frac{1}{9765}$; and that the mean apparent expansion in glass from 32° to 572° F. for each degree is $\frac{1}{11372}$. The temperature in their experiments was estimated by an air thermometer, which they consider more uniform in its rate of expansion than one of mercury. The temperature of 572° F. on the air thermometer corresponds to 586° in the mercurial one.

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* The pressure exerted by equal columns of a fluid, or fluids, is as the density of the columns; and as the density of mercury diminishes with increase of temperature, it follows that a 30-inch column of mercury at 32° F. has a greater weight, or presses more, than a mercurial column of equal base and height at 60°. It is hence necessary, in estimating atmospheric pressure by the barometer, either to have the mercurial column always at the same temperature, or to correct the error arising from difference of temperature by calculation. This correction is effected by finding the length or height of a mercurial column at some standard temperature, as at 60°, which shall exert the same pressure as another column at any other temperature. The formula is thus deduced:—Let H, D, V, be the height, density, and volume of a mercurial column at 32°; and H′, D′, V′, its height, density, and volume when the temperature rises above 32° by any number of degrees expressed by T°. Now it is a principle in hydrostatics that the height of fluid columns of equal pressure is inversely as their density, so that $\frac{H}{H'}=\frac{D'}{D}$; and

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of heat cause a greater dilatation at high than at low temperatures. Thus, if a fluid is heated from 32° to 122°, it will not expand so much as it would do in being heated from 122° to 212°, though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13.4 to 15; in alcohol as 10.9 to 15; and in pure water as 4.7 to 15. Attempts have been made to discover a law by which this progression is regulated, and Dalton conceives that the expansion observes the ratio of the square of the temperature estimated from the point of congelation, or of greatest density; but this opinion is merely hypothetical, and has been shown by Dulong and Petit to be inconsistent with the facts established by their experiments.

There is a peculiarity in the effect of heat upon the bulk of some fluids; namely, that at a certain temperature increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of heat is only observable in those liquids which acquire an increase of bulk in passing from the liquid to the solid state, and is remarked only within a few degrees of temperature above their point of congelation. Water is a noted example of it. Ice, as every one knows, swims upon the surface of water, and, therefore, must be lighter than it, which is a convincing proof that water, at the moment of freezing, must expand. The increase is estimated by Boyle at about $\frac{1}{9}$th of its volume, which gives 900 as the specific gravity of ice, that of water being 1000. (Experiments on Cold.) Dalton estimates the specific gravity of ice at 9.42.

The most remarkable circumstance attending this expansion, is the prodigious force with which it is effected. Boyle filled a brass tube, three inches in diameter, with water, and confined it by means of a moveable plug; the expansion, when it froze, took place with such violence as to push out the plug, though preserved in its situation by a weight equal to 74 pounds. The

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since the volume of the same liquid is also inversely as its density, $\frac{V}{V'}=\frac{D'}{D}$. Consequently, the heights are directly as the volumes, or $\frac{H}{H'}=\frac{V}{V'}$. Since, therefore, $V'=V+V\times\frac{T^v}{9990}$, so is $H'=H+H\times\frac{T^v}{9990}=H.\left(1+\frac{T'}{9990}\right)=H.\left(\frac{9990+T^v}{9990}\right)$. The value of H. is, of course, found by the formula $H=H'\left(\frac{9990}{9990+T^v}\right)$. If, in the formula for H', we substitute for H and T^v their value as stated in the text, we shall find $H'=30.\left(\frac{9990+28}{9990}\right)=30{\cdot}084$, which is the length of a mercurial column at 60°, having the same pressure as a column of mercury at 32°.

The rate of the *actual* and not *apparent* expansion is used in these formulæ, because the length of the mercurial column, depending on atmospheric pressure, is not affected by the expansion or contraction of the tube.

Florentine Academicians burst a hollow brass globe, whose cavity was only an inch in diameter, by freezing the water with which it was filled; and it has been estimated that the expansive power necessary to produce such an effect was equal to a pressure of 27,720 pounds weight. Major Williams gave ample confirmation of the same fact by some experiments which he performed at Quebec in the years 1784 and 1785. (Philosophical Transactions of Ed. ii. 23.)

But it is not merely during the act of congelation that water expands; for it begins to dilate considerably before it actually freezes. Dr. Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. It may be rendered obvious to any one by the following experiment. Fill a flask, capable of holding three or four ounces, with water at the temperature of 60°, and adapt to it a cork, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water will fall in the tube, marking contraction; but in a short time an opposite movement will be perceived, indicating that dilatation is taking place, while the water within the flask is at the same time yielding heat to the freezing mixture in which it is immersed.

To the inference deduced from this experiment, it was objected by some philosophers, that the ascent of the water in the tube did not arise from any expansion in the liquid itself, but from a contraction of the flask, by which its capacity was diminished. In fact, this cause does operate to a certain extent, but it is by no means sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr. Hope, that water does really expand previous to congelation.* He believes the greatest density of water to be between thirty-nine and a half and forty degrees of Fahrenheit's thermometer; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40°, after which the abstraction of heat produces increase instead of diminution of volume. According to Hallstrom, whose experiments are the most recent, and appear to have been conducted with great care, the maximum density of water is 39.39° F. (An. de Ch. et de Ph. xxviii. 90.)

The cause of the expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystallized water, and during its formation the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120°, and consequently occupy more space than when liquid. This may be seen by examining the surface of water while freezing in a saucer. No very satisfactory reason can be assigned for the expansion which takes place previous to congelation. It is supposed, indeed, that the water begins to arrange itself in the order it will assume in the solid state before actually laying aside the liquid form; and this explanation is generally admitted, not so much because it has been proved to be true, but because no better one has been offered.

Water is not the only liquid which expands under reduction of temperature, as the same effect has been observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes, it suffers a very great contraction.

As the particles of air and aëriform substances are not held together by cohesion, it follows that increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of heat much more than solids or liquids. Now, chemists are in the habit of estimating the quantity of the gases employed in their experiments by measuring them; and since the volume occupied by any gas is so much influenced by temperature, it is essential to accuracy that a due correction be made for the variations arising from this cause; that they should know how much dilatation is produced by each degree of the thermometer, whether the rate of expansion is uniform at all temperatures, and whether that ratio is the same in all gases.

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* Philosophical Transactions of Edinburgh, v. 379.

This subject had been unsuccessfully investigated by several philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time. Dalton's method of operating (Manchester Memoirs, vol. v.) was exceedingly simple. He filled with dry mercury a graduated tube, closed at one end and carefully dried; and then, plunging the open end of the tube into a mercurial trough, introduced a portion of dry air. After having marked the bulk and temperature of the air, he exposed it to a gradually increasing heat, the exact amount of which was regulated by a thermometer, and observed the dilatation occasioned by each increase of temperature. The apparatus of Gay-Lussac (An. de Ch. v. 43) was the same in principle, but more complicated, in consequence of the precautions he took to avoid every possible source of fallacy.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of heat, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. Now it appears from the experiments of Gay-Lussac, that 100 parts of air, in being heated from 32° to 212° F., expand to 137·5 parts. The increase for 180 degrees is, therefore, 0.375 or $\frac{37\cdot5}{100}$ths of its bulk; and by dividing this number *by 180, it is found* that a given quantity of dry air dilates to $\frac{1}{480}$th of the volume it occupied at 32°, for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas to occupy 20 measures of a graduated tube at 32°, it may be desirable to determine what would be its bulk at 42°. For every degree of heat it has increased by $\frac{1}{480}$th of its original volume, and, therefore, since the increase amounts to ten degrees, the 20 measures will have dilated by $\frac{10}{480}$ths. The expression will, therefore, be $20+20\frac{10}{480}=20{\cdot}416$. It must not be forgotten that the volume which the gas occupies at 32° is a necessary element in all such calculations. Thus, having 20·416 measures of gas at 42°, the corresponding bulk for 52° cannot be calculated by the formula $20{\cdot}416+20{\cdot}416\times\frac{10}{480}$; the real expression is $20.416+20\times\frac{10}{480}$, because the increase is only $\frac{10}{480}$ths of the space occupied at 32°, which is 20 measures.*

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* The following are convenient general formulæ for these calculations:— Let P' be the volume of gas at any temperature above 32°, T' the number of degrees above that point, and P its volume at 32°. Then $P'=P.\left(1+\frac{T'}{480}\right)=P.\left(\frac{480+T'}{480}\right)$; and if P is unknown, its value, deduced from the last equation, may be calculated from the formula $P=P'.\left(\frac{480}{480+T'}\right)$.

It frequently happens, in the employment of Fahrenheit's thermometer, that when P' for the above formula is known, it is not P itself which is wanted, but the volume of gas at some other temperature, as at 60° F. This value may be obtained without first calculating what P is. Thus, retaining the value of P' and T' as in the preceding formula, let P'' be the corresponding quantity of gas at some other temperature, the degrees of which above 32° may be expressed by T''. Now $P''=\frac{(480+T'')}{480}\times P$; but as P

A similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

The rate of expansion of atmospheric air at temperatures exceeding 212° has been examined by Dulong and Petit, and the following table contains the result of their observations. (An. de Ch. et de Ph. vii. 120.)

Temperature by the Mercurial Thermometer.		Corresponding volumes of a given volume of air.
Fahrenheit.	Centigrade.	
— 33	— 36	0.8650
32	0	1.0000
212	100	1.3750
302	150	1.5576
392	200	1.7389
482	250	1.9189
572	300	2.0976
Mercury boils 680	360	2.3125

is unknown, let its value in P′ be substituted. Thus, $P''=\left(\frac{480+T''}{480}\right)\times\left(\frac{P'480}{480+T'}\right)$; which gives $P''=\frac{480^2\ P'+480\ T''\ P'}{480^2+480\ T'}=\frac{P'480\,(480+T'')}{480\ (480+T')}=\frac{P'\ (480+T'')}{480+T'}$.

Suppose, for example, a portion of gas occupies 100 divisions of a graduated tube at 48°, how many will it fill at 60° F.? Here $P'=100$; $T'=48-32$, or 16; $T''=60-32$, or 28. The number sought, or the $P''=\frac{100\times508}{496}=102.42$.*

* To those who are not algebraists, the following explanation and calculation may be useful. As every gas expands 1-480th of the volume it would occupy at 32°, for every degree of Fahrenheit's thermometer, it is clear that it will expand 1-481st part of its volume at 33°, 1-482d part of its volume at 34°, and so on for each successive addition of one degree of caloric. In order to know, therefore, the fractional dilatation of a gas at any temperature above 32°, for a single degree, it is only necessary to add to the denominator of the fraction 1-480, a number of units equal to the number of degrees that the gas exceeds the temperature of 32°. Thus a gas at the temperature of 42° will expand 1-490th, at 52° 1-500, of its volume, for every increment of heat equal to one degree. Knowing in this simple manner the fractional amount of expansion of a gas at any temperature for one degree, we multiply this amount by the difference between the existing temperature and the temperature to which it is desired to reduce the volume. If the reduction is to a higher temperature, this product is added to the existing volume; if to a lower, subtracted. Thus, to calculate the example which Dr. Turner has selected, namely, 100 measures of a gas at 48°, what will be its bulk at 60°, we proceed as follows: as the existing temperature is 16° above 32°, its fractional expansion for one degree will be $1\text{-}\overline{480+16}=1\text{-}496$. Taking the 496th part of one hundred, the given volume, we have the actual expansion

Hydrogen gas was found to expand in the same proportion; so that all gases may be inferred to expand to the same extent, for equal increments of heat, between —33° F. and 680°; and the same law probably prevails at all temperatures.*

THERMOMETERS.

The influence of heat over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but in general return exactly to their original volume when the heat is withdrawn. The first attempt to measure the intensity of heat on this principle was made early in the 17th century, and the honour of the invention is by some bestowed on Sanctorius, by others on Cornelius Drebel, and by others on the celebrated Galileo. The material used by Sanctorius was atmospheric air. The construction of the thermometer itself, or *thermoscope* as it was sometimes called, is exceedingly simple. A glass tube is to be selected for the purpose, and one end of it is blown out into a spherical cavity, while its other extremity is left open. After expelling a small quantity of air by heating the ball gently, the open end of the tube is plunged into coloured water, and a portion of the liquid is forced up into the tube by the pressure of the atmosphere, as the air within the ball contracts. In this state it indicates changes of temperature with extreme delicacy, the alternate expansion and contraction of the confined air being rendered visible by the corresponding descent and ascent of the coloured water in the stem. The material used in its construction, also, is peculiarly appropriate; because air, like all gases, expands uniformly by equal increments of heat. There are, however, two forcible objections to the general employment of this thermometer. In the first place, its dilatations and contractions are so great, that it is inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure as well as by heat, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.

For the reasons just stated, the common air thermometer is rarely employed; but a modification of it, described in 1804 by Sir J. Leslie, in his Essay on Heat, under the name of *Differential Thermometer*, is entirely free from the last objection, and is admirably fitted for some special purposes. This instrument was invented a century and a half ago by Sturmius, Professor of Mathematics at Altdorff, who has left a description and sketch of it in his *Collegium Curiosum*, p. 54, published in the year 1676; but like other air thermometers it had fallen into disuse, till it was again brought into notice by Leslie. As now made it consists of two thin glass

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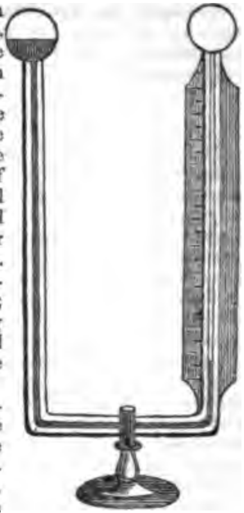
for one degree. This, upon calculation, will be found to be .2016, which, multiplied by 12, the difference between the actual temperature and the temperature of the volume sought, will give 2.419, as the actual expansion, corresponding to 12 degrees. As the temperature of the volume sought is above the original temperature, this number must be added to the given volume. So that $100+2{\cdot}419=102{\cdot}419$ will be the volume sought. *Ed.*

* The law of the equable expansion or contraction of gases by equal increments or decrements of heat is a very curious one; but it becomes particularly so when viewed in connexion with a descending temperature. If gases expand or contract 1-480th of the volume they occupy at the freezing point, for every alteration of temperature equal to one degree, it is obvious that a given volume of any gas at 32° will be *expanded* by a volume equal to itself, by having its temperature raised 480°. But the converse of the proposition would seem to involve a paradox; for by the application of the same law, a given volume of any gas at 32°, if cooled down to 480°, would be *contracted* by a volume equal to itself, that is, reduced to nothing. *Ed.*

balls joined together by a tube, bent twice at a right angle, as represented in the annexed figure. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls; for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surfaces of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected; for the elasticity of the air on one side being then greater than that on the other, the liquid will retreat towards the ball whose temperature is the lowest.



Solid substances are not better suited to the construction of a thermometer than gases; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids which expand more than the one and less than the other, are exempt from both extremes; and, consequently, we must search among them for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury, and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of heat than other liquids, while its dilatations between 32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of heat does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass; and, therefore, if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

The first object in constructing a thermometer is to select a tube with a very small bore, which is of the same diameter through its whole length; and then, by melting the glass, to blow a small ball at one end of it. The mercury is introduced by rarefying the air within the ball, and then dipping the open end of the tube into that liquid. As the air cools and contracts, the mercury is forced up, entering the bulb to supply the place of the air which had been expelled from it. Only a part of the air, however, is removed by this means; the remainder is driven out by the ebullition of the mercury.

Having thus contrived that the bulb and about one-third of the tube shall be full of mercury, the next step is to seal the open end hermetically. This is done by heating the bulb till the mercury rises very near the summit, and then suddenly darting a fine-pointed flame from a blow-pipe across the opening, so as to fuse the glass and close the aperture before the mercury has had time to recede from it.

The construction of a thermometer is now so far complete that it affords a means of ascertaining the comparative temperature of bodies; but it is deficient in one essential point, namely, the observations made with different instruments cannot be compared together. To effect this object, the thermometer must be graduated, a process which consists of two parts. The first and most important is to obtain two fixed points which shall be the same in every thermometer. The practice now generally followed for this purpose was introduced by Newton, and is founded on the fact, that when a thermometer is plunged into ice that is dissolving, and into water which is boiling, it constantly stands at the same elevations in all countries, provided there is a certain conformity of circumstances. The point of congelation is easily determined. The instrument is to be immersed in snow or pounded ice, which is liquefying in a moderately warm atmosphere, till the mercury becomes stationary. To fix the boiling point is a more delicate operation; since the temperature at which water boils is affected by various circumstances which will be more particularly mentioned hereafter. It is sufficient to state the general directions at present;—that the water be perfectly pure, free from any foreign particles, and not above an inch in depth,—the ebullition brisk, and conducted in a deep metallic vessel, so that the stem of the thermometer may be surrounded by an atmosphere of steam, and thus exposed to the same temperature as the bulb—the vapour be allowed to escape freely—and the barometer stand at 30 inches.

The second part of the process of graduation consists in dividing the interval between the freezing and boiling points of water into any number of equal parts or degrees, which may be either marked on the tube itself, by means of a diamond, or first drawn upon a piece of paper, ivory, or metal, and afterwards attached to the thermometer. The exact number of degrees into which the space is divided, is not very material, though it would be more convenient did all thermometers correspond in this respect. Unfortunately this is not the case. In Britain we use Fahrenheit's scale, and accordingly in this treatise the degrees always refer to that scale, except when the contrary is directly expressed; whereas the continental philosophers employ either the centigrade, or that of Reaumur. The centigrade is the most convenient in practice; its boiling point is 100, that of melting snow is the zero, or beginning of the scale, and the interval is divided into 100 equal parts. The interval in the scale of Reaumur is divided into 80 parts, and in that of Fahrenheit into 180; but the zero of Fahrenheit is placed 32 degrees below the temperature of melting snow, and on this account the point of ebullition is 212°.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Reaumur's thermometer. Fahrenheit's is, therefore, reduced to the centigrade scale, by multiplying by five, and dividing by nine, or to that of Reaumur, by multiplying by four instead of five. Either of these may be reduced to Fahrenheit by reversing the process; the multiplier is nine in both cases, and the divisor four in the one and five in the other. But it must be remembered in these reductions, that the zero of Fahrenheit's thermometer is 32 degrees lower than that of the centigrade or Reaumur, and a due allowance must be made for this circumstance. An example will best show how this is done. To reduce 212° F. to the centigrade, first subtract 32, which leaves 180; and this number multiplied by $\frac{5}{9}$, gives the corresponding expression in the centigrade scale. Or to reduce 100° C. to Fahrenheit, multiply by $\frac{9}{5}$, and then add 32. To save the trouble of such reductions, I have subjoined a table, which shows the degrees on the centigrade scale and that of Reaumur, corresponding to the degrees of Fahrenheit's thermometer.

Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.
212	100	80	113	45	36	14	-10	- 8
203	95	76	104	40	32	5	-15	-12
194	90	72	95	35	28	- 4	-20	-16
185	85	68	86	30	24	-13	-25	-20
176	80	64	77	25	20	-22	-30	-24
167	75	60	68	20	16	-31	-35	-28
158	70	56	59	15	12	-40	-40	-32
149	65	52	50	10	8			
140	60	48	41	5	4			
131	55	44	32	0	0			
122	50	40	23	-5	-4			

The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees above and below those points. But as mercury freezes at 39 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which has been used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory. Mercury is preferable to any other liquid; but even its indications cannot be altogether relied on. For, in the first place, its expansion for equal increments of heat is greater at high than at low temperatures; and, secondly, glass expands at temperatures beyond 212° in a more rapid ratio than mercury, and consequently, from the proportionally greater capacity of the bulb, the apparent expansion of the metal is considerably less than its actual dilatation. Thus Dulong and Petit observed, that when the air thermometer is at 572°, the common mercurial thermometer stands at 586°; but when corrected for the error caused by the glass, it indicates a temperature of 597·5°. No liquid can be employed for temperatures which exceed 662°, since all of them are then either dissipated in vapour, or decomposed.

M. Bellain has observed that mercurial thermometers slowly change their point of zero, which uniformly becomes higher than at the time of graduation. This phenomenon appears owing to a diminished capacity of the bulb due to the atmosphere continually pressing on its exterior, while a vacuum exists in the interior of the tube; for it has not been noticed either in mercurial thermometers which are unsealed, or in thermometers made with alcohol. The principal contraction ensues soon after the tube is sealed, and hence some months should be permitted to elapse between the sealing and graduation of a thermometer. (An. de Ch. et de Ph. xxi. 330.)

The instruments for measuring intense degrees of heat are called *pyrometers*, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The action of most pyrometers depends on the elongation of a metallic bar by heat; and the difficulty in their construction consists in finding an infusible metal of uniform expansibility, and in measuring the degree of expansion with exactness. This subject has for some time occupied the attention of Professor Daniell, who has at last succeeded in forming a pyrometer which, with a little practice, may be used with facility, and appears susceptible of very great precision. (Phil. Trans. 1830 and 31.) This instrument consists of two parts, the *Register* and *Scale*, the former designed for exposure to the heat to be estimated, and the latter for measuring the exact amount of expansion. The first consists of a bar of black-lead earthenware, in which is drilled a hole 3-10ths of an inch in diameter, and 7½ inches deep. Into this hole a cylindrical bar of platinum or soft iron, of nearly the same diameter, and 6½ inches long, is introduced, so as to rest against the solid end of the hole; and upon the outer or free end of the metallic bar rests a cylindrical piece of porcelain, called the index, 1½ inches long, and is kept firmly in its place by a strap of platinum and a little wedge of earthenware. The object of this arrangement is, that when the register is heated, the metal expanding at each temperature more than the earthenware case, presses forward the index; and as this last moves with friction in consequence of the strap and wedge, it remains in its place when the register is removed from the fire and cooled. The scale is an instrument designed for measuring with minute accuracy the precise extent to which the index has been pushed forward by the metallic bar. It thus indicates the apparent elongation of the bar, that is, the difference between its elongation and that of the black-lead case which contains it. For its indications to be correct, that is, in order that equal dilatations should indicate equal increments of heat, it is necessary that the bar and its case should both expand uniformly, or both vary at the same rate. Now in regard to the black-lead case, its total expansion is so very small, that any want of uniformity at intermediate points cannot be detected; but since, as will shortly be more fully stated, all earthenware and other argillaceous substances contract when first heated, the case must not be used in pyrometry, until it has been exposed in close vessels to at least as high a temperature as that which will afterwards be employed. As for the expansions of the metallic bar, these are not exactly uniform (page 18); but still they afford a good practical index of the relative intensity of different fires, and will be an exact measure of temperature when the precise rate of expansion shall have been determined.

The pyrometer of Wedgwood acts on a different principle, being founded on the property which clay, a compound of aluminous earth and water, possesses of gradually losing its water when exposed to an increasing temperature, and of contracting as the water is dissipated. The contraction even continues after every trace of water has been removed, owing to partial vitrification occurring, which tends to bring the particles of the clay into still nearer proximity. The intensity of the heat may, therefore, in some measure be estimated by the degree of contraction which it has occasioned.

The apparatus consists of a metallic groove, 24 inches long, the sides of which converge, being half an inch wide above, and three-tenths below. The clay, well washed, is made up into little cylinders or truncated cones which fit the commencement of the groove, after having been heated to redness; and their subsequent contraction by heat is determined by allowing them to slide from the top of the groove downwards, till they arrive at a part of it through which they cannot pass. Mr. Wedgwood divided the whole length of the groove into 240 degrees, each of which he supposed equal to 130 of Fahrenheit; and he fixed the zero of his scale at the 1077th degree of Fahrenheit's thermometer.

Wedgwood's pyrometer is no longer employed by scientific men, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second piece, from the same heat, will be exactly similar to that of the first; especially as it is difficult to procure specimens of the earth, the composition of which is in every respect the same. It is doubtful, too, if its point of zero has been correctly estimated; and Guyton de Morveau has shown that each degree corresponds rather to 62.5 than to 130 degrees of Fahrenheit.

For some purposes, especially in making meteorological observations, it is a very desirable object to ascertain the highest and lowest temperature which has occurred in a given interval of time, during the absence of the observer. The instrument employed with this intention is called a *Register Thermometer*, and the most convenient kind with which I am acquainted, is that described in the Philosophical Transactions of Edinburgh, iii. 245, by Dr. John Rutherford. The thermometer for ascertaining the most intense cold is made with alcohol, and the bulb is bent at a right angle to the stem, so that the latter may conveniently be placed in a horizontal position. In the spirit is immersed a cylindrical piece of black enamel, of such size as to move freely within the tube. In order to make an observation, the enamel should be brought down to the surface of the spirit, an object easily effected by slight percussion while the bulb is inclined upwards. When the thermometer sinks by exposure to cold, the enamel likewise retreats towards the bulb, owing to its adhesion to the spirit; but, on expanding, the spirit passes readily beyond the enamel, leaving it at the extreme point to which it had been conveyed by the previous contraction.

For registering the highest temperature, a common mercurial thermometer of the same form as the preceding is employed, having a small cylindrical piece of black enamel at the surface of the mercury. When the mercury expands, the enamel is pushed forward; and as the stem of the thermometer is placed horizontally, it does not recede when the mercury contracts, but remains at the spot to which it had been conveyed by the previous dilatation. The enamel is easily restored to the surface of the mercury by slight percussion while the bulb is inclined downwards; but this should be performed with care, lest the enamel, in falling abruptly, should interrupt the continuity of the mercurial column, and interfere with the indications of the instrument. The risk of this accident is lessened by putting some pure naphtha in the tube beyond the mercury, and its presence is likewise of use in preventing the oxidation of the mercury. The above description applies to an improvement on Dr. Rutherford's thermometer, made by Mr. Adie of Edinburgh.

Though the thermometer is one of the most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point out a difference in the temperature of two or more substances with great nicety; but it does not indicate how much heat any body contains. It does not follow, because the thermometer stands at the same elevation in any two bodies, that they contain equal quantities of heat; nor is it right to infer that the warmer possesses more of this principle than the colder. The thermometer gives the same kind of information which may be discovered, though less accurately, by the feelings; it recognizes in bodies that state of caloric alone, which affects the senses with an impression of heat or cold,—the condition expressed by the word *temperature*. All we learn by this instrument is, whether the temperature of one body is greater or less than that of another; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of heat present in bodies.

Very little reflection will evince the propriety of these remarks. If two glasses of unequal size be filled with water just taken from the same spring, the thermometer will stand in each at the same height, though their quantities of heat are certainly unequal. This observation naturally suggests the inquiry, whether different kinds of substances, whose temperatures as estimated by the thermometer are the same, contain equal quantities of heat,—if, for example, a pound of iron contains as much heat as a pound of water or mercury. The foregoing remark shows that equality of temperature is not necessarily connected with equality in quantity of heat; and the inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° and the other at 50°, the temperature of the mixture will be the arithmetical mean or 75°; that is, the 25 degrees lost by the warm water will exactly suffice to heat the cold water by the same number of degrees. It is hence inferred, that equal weights or measures of water of the same temperature contain equal quantities of heat; and the same is found to be true of other bodies. But if equal weights or equal bulks of *different* substances are employed, the result will be different. Thus if a pint of mercury at 100° be mixed with a pint of water at 40°, the mixture will have a temperature of 60°, so that the 40 degrees lost by the former, heated the latter by 20 degrees only; and when, reversing the experiment, the water is at 100° and the mercury at 40°, the mixture will be at 80°, the 20 degrees lost by the former causing a rise of 40 in the latter. The fact is still more strikingly displayed by substituting equal weights for measures. For instance, on mixing a pound of mercury at 160° with a pound of water at 40°, a thermometer placed in the mixture will stand at 45°; but if the mercury be at 40° and the water at 160°, the mixture will have a temperature of 155°. If water at 100° be mixed with an equal weight of spermaceti oil at 40°, the mixture will be found at 80°; and when the oil is at 100° and the water at 40°, the temperature of the mixture will be only 60°.

It appears from the facts just stated, that the same quantity of heat imparts twice as high a temperature to mercury as to an equal volume of water; that a similar proportion is observed with respect to equal weights of spermaceti oil and water; and that the heat which gives 5 degrees to water will raise an equal weight of mercury by 115 degrees, being the ratio of 1 to 23. Hence if equal quantities of heat be added to equal weights of water, spermaceti oil, and mercury, their temperatures in relation to each other will be expressed by the numbers 1, 2, and 23; or, what amounts to the same, in order to increase the temperature of equal weights of those substances to the same extent, the water will require 23 times as much heat as the mercury, and twice as much as the oil. The peculiarity exemplified by these substances, and which it would be easy to illustrate by other examples, was first noticed by Dr. Black. It is a law admitted to be universal, and may be thus expressed; that *equal* quantities of different bodies require *unequal* quantities of heat to heat them equally. This difference in bodies was expressed in the language of Dr. Black by the term *capacity* for heat, a word apparently suggested by the idea that the heat present in any substance is contained within its pores, or in the spaces left between its particles, and that the quantity of heat is regulated by the size of the pores. And indeed at first view there appear sufficient grounds for this opinion; for it is observed, that very compact bodies have the smallest capacities for heat, and that the capacity of the same substance often increases as its density becomes less. But, as Black himself pointed out, if this were the real cause of the difference, the capacities of bodies for heat should be inversely as their densities. Thus, since mercury is thirteen times and a half denser than water, the capacity of the latter for heat ought to be only thirteen times and a half greater than the former, whereas it is twenty-three times as great. Oil occupies more space than an equal weight of water, and yet the capacity of the latter for heat is double that of the former. The word capacity, therefore, is apt to excite a wrong notion, unless it be carefully borne in mind, that it is merely an expression of the fact without allusion to its cause; and to avoid the chance of error from this source, the term *specific heat* has been proposed as a substitute for it, and is now very generally employed.

The singular fact of substances of equal temperature containing unequal quantities of heat naturally excites speculation about its cause, and various attempts have been made to account for it. The explanation deduced from the views of Black is the following. He conceived that heat exists in bodies in two opposite states: in one it is supposed to be in chemical combination, exhibiting none of its ordinary characters, and remaining as it were concealed, without evincing any signs of its presence; in the other, it is free and uncombined, passing readily from one substance to another, affecting the senses in its passage, determining the height of the thermometer, and in a word giving rise to all the phenomena which are attributed to this active principle.

Though it would be easy to start objections to this ingenious conjecture, it has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. It is entirely consistent with analogy. For since heat is regarded as a material substance, it would be altogether anomalous were it not influenced, like other kinds of matter, by chemical affinity; and if this be admitted, it ought certainly, in combining, to lose some of the properties by which it is distinguished in its free state. According to this view, it is intelligible how two substances, from being in the same condition with respect to free heat, may have the same temperature; and yet that their actual quantities of heat may be very different, in consequence of one containing more of that principle in a combined or latent state than the other. But in admitting the plausibility of this explanation, it is proper to remember that it is at present entirely hypothetical; and that the language suggested by an hypothesis should not be unnecessarily associated with the phenomena to which it owes its origin. Accordingly, the word *sensible* is better than *free* heat, and *insensible* preferable to *combined* or *latent* heat; for by such terms the fact is equally well expressed, and philosophical propriety strictly preserved.*

It is of importance to know the specific heat of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of heat requisite for heating them by the same number of degrees. Thus the caloric required to heat equal quantities of water, spermaceti oil, and mercury by one degree, is in the ratio of 23, 11.5, and 1, and, therefore, their specific heats are expressed by those numbers. Water is commonly one of the materials employed in such experiments, as it is customary to compare the specific heat of other bodies with that of water.†

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* The theory of latent heat of Dr. Black, as applied to the explanation of the different specific heats of bodies, would seem in some respects to be unphilosophical. If Pictet's theory of the equilibrium of caloric be admitted, then equality of temperature in any two bodies merely means that their caloric has no tendency to pass from one to the other, without the idea having any necessary connection with the absolute quantity of caloric contained in them. It may be admitted as highly probable that the reason why different bodies assume to themselves unequal quantities of heat, when this principle has assumed a state of rest, is that their affinities for caloric are different; yet it by no means follows, that the caloric in such bodies is in two different states, *sensible* or *free*, and *insensible* or *combined*. If we impart ten degrees of heat to equal weights of water and oil, the water will have received twice as much caloric as the oil. Here the "actual quantities of heat" received are "very different;" but are we on this account to suppose that part of the caloric received by the water is in an insensible or combined state? It will at once be evident that this cannot be the case; for if the equal weights of water and oil, after being heated ten degrees, be allowed to cool equally, the water will lose twice as much actual caloric as the oil. Now all the caloric lost during the cooling becomes free caloric; for it is distributed among surrounding bodies.

The fact is, that the quantity of caloric gained or lost by any number of bodies, in being heated or cooled through the same number of degrees, bears a constant proportion to their several specific heats. Hence to maintain an equality of temperature among any set of bodies, the quantity of caloric contained by each must be directly proportional to its specific heat. Whatever *subverts* this relation will necessarily change the temperature.

It sometimes happens that the loss or gain of caloric by a body is exactly proportional to the change it may undergo in specific heat or capacity. Thus, if a body receive caloric, and have, at the same time, its capacity proportionably increased, its temperature remains the same, though it be constantly receiving caloric; and it is by such cases as these that the doctrine of insensible or combined heat is most plausibly supported. But, upon taking a nearer view of the subject, it will be found that the temperature remains the same in conformity with the principles laid down in this note; for the capacity and heat being simultaneously and proportionably increased, the relation between them, so far from being *subverted*, is maintained.—*Ed.*

† A formula for such calculations is thus deduced:—Let w, t, and s, be the weight, temperature, and specific heat of the warmer body; w', t', and s', the weight, temperature, and specific heat of the colder body; and θ the temperature of the mixture. Then the temperature lost by the warmer body will be expressed by $(t-\theta)$, and its actual loss of heat by $s.\,(t-\theta).\,w$;

This method was first suggested by Black, and was afterwards practised to a great extent by Drs. Crawford and Irvine.* But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of heat which bodies give out in cooling; for if water require 23 times more heat than mercury to raise its temperature by one or more degrees, it must also lose 23 times as much in cooling. The calorimeter, invented and employed by Lavoisier and Laplace, acts on this principle. The apparatus consists of a wire cage, suspended in the centre of a metallic vessel so much larger than itself, that an interval is left between them, which is filled with fragments of ice. The mode of estimating the quantity of heat which is emitted by a hot body placed in the wire cage, depends upon the fact, that ice cannot be heated beyond 32°; since every particle of heat which is then supplied is employed in liquefying it, without in the least affecting its temperature. If, therefore, a flask of boiling water be put into the cage, it will gradually cool, the ice will continue at 32°, and a portion of ice-cold water will be formed; and the same change will happen when heated mercury, oil, or any other substance is substituted for the hot water. The sole difference will consist in the quantity of ice liquefied, which will be proportional to the heat lost by those bodies while they cool; so that their capacity is determined merely by measuring the quantity of water produced by each of them. This is done by allowing the water, as it forms, to run out of the calorimeter by a tube fixed in the bottom of it, and carefully weighing the liquid which issues.

There is one obvious source of fallacy in this mode of operating, against which it is necessary to provide a remedy; namely, the ice not only receives heat from the substance in the central cage, but must also receive it from the air of the apartment in which the experiment is conducted. This inconvenience is avoided by surrounding the whole apparatus by a larger metallic vessel of the same form as the smaller one, and of such a size that a certain space is left between them, which is to be filled with pounded ice or snow. No external heat can now penetrate to the inner vessel; because all the heat derived from the apartment is absorbed by the outer one, and is employed, not in elevating its temperature, but in dissolving the pounded ice within it.

Notwithstanding this precaution, however, the accuracy of the calorimeter may fairly be questioned. For it is essential, in order to obtain correct results, that all the water which is produced should flow out and be collected. But there is reason to suspect that some of the water is apt to freeze again before it has had time to escape; and if this be true, as *à priori* is very probable, then the information given by the calorimeter must be rejected as useless.

The determination of the specific heat of gaseous substances is a problem of importance, and has accordingly occupied the attention of several experimenters of great science and practical skill; but the inquiry is beset with so many difficulties that, in spite of the talent which has been devoted to it, our best results can be viewed as approximations only, requiring to be corrected by future research. Dr. Crawford, to whom we are indebted for the first elaborate investigation of the subject, conducted his experiments in the following manner. He obtained two copper vessels made as light as possible, and exactly of the same form, size, and weight; exhausted one of them, and

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while the temperature acquired by the colder body will be $(\theta - t')$. and the whole heat gained will be represented by $s'.(\theta - t').w'$. As the heat gained by one is equal to that lost by the other, it follows that $s.(t - \theta).w = s'.(\theta - t').w'$; and consequently $\frac{s'}{s'} = \frac{(\theta - t').w'}{(t - \theta).w}$. In case of the weights being equal, or $w = w'$, then $\frac{s}{s'} = \frac{\theta - t'}{t - \theta}$; that is, for equal weights, the specific heats are inversely as the variations of temperature.

* Crawford on Animal Heat, and Irvine's Chemical Essays.

filled the other with the gas to be examined. They were next heated to the same extent by immersion in hot water, and then plunged into equal quantities of cold water of the same temperature. Each flask heated the water; but while the exhausted flask communicated solely the heat of the copper, the other gave out an equal quantity of heat from the metal of which it was made, together with that derived from the gas in its interior. The effect produced by the former deducted from that of the latter gave the heating power of the confined gas, the precise information wanted. By repeating the experiment with air and different gases, their comparative heating powers, or their specific heats, were ascertained. But correct as is the leading principle on which these experiments were founded, the results are now universally admitted to be very wide of the truth, and, therefore, it can answer no useful purpose to cite them. The fallacy is attributable to the circumstances of the heat derived from the containing vessel being so great compared to that emitted by the confined gas, that the effect ascribed to the latter is confounded with, and materially influenced by, the unavoidable errors of manipulation.

The same subject was investigated by Lavoisier and Laplace by means of their calorimeter. A current of gas was transmitted in a serpentine tube through boiling water in order to be heated, and was then made to circulate within the calorimeter in a similar tube surrounded with ice. Its temperature in entering and quitting the calorimeter was ascertained by thermometers, and the heat lost by each gas was estimated by the quantity of ice liquefied. Their experiments are of course liable to the objections already made to the use of ice; but a similar train of experiments, not exposed to this fallacy, was conducted in the year 1813 with extreme care by Delaroche and Bérard. (An. de Chimie, LXXXV. and Annals of Phil. II.) They transmitted known quantities of gas, heated to 212°, in a uniform current through the calorimeter; and, instead of ice, surrounded the serpentine tube with water, the temperature of which, as well as of the gas at its exit, was ascertained during the course of the process by delicate thermometers. By operating with a considerable quantity of gas, they avoided the error into which Crawford fell; and the experiments, though complicated and involving various sources of error, were conducted with such skill and caution that they inspired great confidence, and are still admitted to be more accurate than any which have been made on this difficult subject. Their results are contained in the following table; the specific heat of the gases being referred to atmospheric air as unity in the two first columns, and to water in the third.

Names of Substances.	Under equal Volumes.	Under equal Weights.	
Atmospheric air	1.0000	1.0000	0.2669
Hydrogen gas	8.9033	12.3400	3.2936
Oxygen gas	0.9765	0.9848	0.2361
Nitrogen gas	1.0000	1.0318	0.2754
Nitrous oxide gas	1.3503	0.8878	0.2369
Olefiant gas	1.5530	1.5763	0.4207
Carbonic oxide gas	1.0340	1.0805	0.2884
Carbonic acid gas	1.2583	0.8280	0.2210
Water	. .	. . . . .	1.0000
Aqueous vapour	. .	. . . . .	0.8470

Some experiments performed by Clement and Desormes, and published in the year 1819 in the *Journal de Physique*, LXXXIX. 320, were confirmatory of the foregoing results; and Dalton, in the second volume of his *Chemical Philosophy*, page 282, states that he has repeated the experiment of Delaroche and Bérard on the specific heat of atmospheric air, and is convinced of their estimate being very near the truth. But the accuracy of their results has been questioned by others, and some of the objections are by no means deficient in force. One of these was stated by Mr. Haycraft in the Edinburgh Phil. Trans for 1824, namely, that the gases were employed in a moist instead of a dry state, a circumstance which would doubtless in some measure modify the result; and others have been mentioned by De la Rive and Marcet. (An. de Ch. et de Ph. xxxv. 5. and xli. 78.) For example, the precise temperature of the gases used in their experiments was not ascertained in an unexceptionable manner; because a thermometer surrounded by gaseous matter is affected, not only by contact with the gas itself, but likewise by the radiant heat emitted or absorbed by the containing vessel. It is also to be remarked that the heated gases, in passing through the calorimeter, diminished in volume in proportion as they cooled. Now it is found invariably that whenever the bulk of a gas is diminished, a certain portion of insensible heat becomes sensible; so that in the experiments of Delaroche and Bérard, the heating influence of the gases was a complex phenomenon, partly dependent on the heat lost in cooling, and partly on that developed by the accompanying diminution in volume. This last source of heat ought to have been avoided, and in the experiments of Crawford it was so; for the heated gases with which he operated, being confined in a close vessel, underwent no change of volume while they cooled, though of course their elasticity was thereby diminished.

These considerations induced De la Rive and Marcet to undertake this difficult inquiry. In their experiments the gases were confined in a thin globe of glass, and the temperature was estimated, not by a thermometer, but by the elastic force communicated by the heat, according to the law of Dalton and Gay-Lussac already mentioned. (Page 21.) The glass vessel was placed in the centre of a very thin copper globe, the inner surface of which was made to radiate freely by a coating of lamp-black, and the air between it and the glass globe was withdrawn by an air-pump. The whole apparatus being brought to the temperature of 68°, was immersed during exactly five minutes in water kept steadily at 86°; and the heat imparted to the copper was radiated from its inner surface, and thus reached the glass globe in the centre. By always operating exactly in the same manner, it was conceived that the same volume of each gas would receive equal quantities of heat in equal times; and that from the temperature thus communicated to each, its specific heat might be inferred. In two sets of experiments thus conducted, they found that each gas acquired the same elasticity, or was heated to the same degree; and thence they inferred that gases in general, for equal volumes and pressures, have the same capacity for heat. They also operated with the same gas at different densities; and concluded that the specific heat of each gas, for equal volumes, diminishes slowly as its density decreases.

In the *An. de Ch. et de Ph.* xli. 113, Dulong has published some critical remarks on these experiments. He argues, in the first place, that the quantity of gas employed was so small, that any effect arising from a difference in specific heat could not be appreciated. He contends, further, that the temperature acquired by a gas in such experiments is not influenced by its specific heat only, but in part by the relative facility with which heat is transmitted through the gas. It has been already observed that heat is conducted by gaseous matter with extreme slowness, but is rapidly diffused through it in consequence of the mobility of its particles. Now gases differ considerably under this point of view. Hydrogen acquires the temperature of a hot body placed in it much more rapidly than carbonic acid; and, therefore, were the same volume of these gases exposed for an equal short period to equal sources of heat, the former would acquire a higher temperature simply from its conveying heat more readily. The validity of these strictures can scarcely, I apprehend, be denied. It may, therefore, be inferred from the foregoing observations, that the specific heats of the gases are not yet accurately known, and that the numbers stated by Delaroche and Bérard are probably the best approximations hitherto published.

The circumstances which merit particular notice, concerning the specific heat of bodies, may be arranged under the eight following heads:—

1. Every substance has a specific heat peculiar to itself; whence it follows, that a change of composition will be attended by a change of capacity for heat.

2. The specific heat of a body varies with its form. A solid has a smaller capacity for heat than the same substance when in the state of a liquid; the specific heat of water, for instance, being 9 in the solid state, and 10 in the liquid. Whether the same weight of a body has a greater specific heat in the solid or liquid form than in that of vapour, is a circumstance not yet decided. The only experiments in point are those of Crawford, and Delaroche and Bérard. The former estimated the specific heat of vapour at 1.55, and the French philosophers at 0.847, compared to that of water as unity; nor is it possible to say which of these widely discordant results is nearer the truth, as neither can be relied on with confidence.*

3. When a given weight of any gas is made to vary in density and volume while its elasticity is unchanged, as when air confined in a tube over mercury is heated and suffered to expand without variation of pressure, the specific heat is believed to remain constant. Gaseous matter, being free from the disturbing agency of cohesion, is very equably influenced by heat: according to our best observations, equal increments of heat, when the elasticity is constant, give rise both to equal increments of temperature and equal expansions.

4. Of the specific heat of equal volumes of the same gas at a varying density and elasticity, as when air is forced into a bottle with different degrees of force, nothing certain has been established; for the experiments of De la Rive and Marcet, above described, have led to no decisive conclusion.

5. The specific heat of equal weights of the same gas varies as the density and elasticity vary. Thus, when 100 measures of air expand by diminished pressure to 200 measures, its specific heat is increased; and when the same quantity of air is compressed into the space of 50 measures, its specific heat is diminished. The exact rate of increase is unknown; but according to Delaroche and Bérard, the ratio is less rapid than the diminution in density; that is, the specific heat of any gas being 1, it is not 2, but between one and two, when its volume is doubled.

6. The specific heat of solids and liquids was formerly thought, especially by Drs. Crawford and Irvine, to be constant at all temperatures, so long as they suffer no change of form or composition. Dr. Dalton, however, (Chemical Philosophy, part I. p. 50,) endeavours to show that the specific heat of such bodies is greater in high than at low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them. Thus the mean specific heat of iron between

0°	Centigrade and	100° Centigrade is	0.1098
0°	. .	200° . .	0.1150
0°	. .	300° . .	0.1218
0°	. .	350° . .	0.1255

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* The question here referred to may not be decided experimentally with rigid accuracy, and yet it is decided with much plausibility by the admitted doctrine of the formation of vapours from liquids, and the increased specific heat of vapours by rarefaction. Dr. Turner admits that the specific heat of water in the liquid state is greater than in that of ice. Is it not probable then that the specific heat of steam is greater than that of an equal weight of water? Conceding that the increased capacity that takes place as water changes into steam, is not conclusive as to the increased specific heat of the steam itself after having been formed; yet as a separation of the particles of steam by rarefaction is admitted to increase its specific heat, à fortiori the greater separation of the aqueous particles in passing from water to steam might be supposed to be attended with the same result.—*Ed.*

And the same is true of the substances contained in the following table.

	Mean Capacity between 0° and 100° C.	Mean Capacity between 0° and 300° C.
Mercury	0.0330	0.0350
Zinc	0.0927	0.1015
Antimony	0.0507	0.0549
Silver	0.0557	0.0611
Copper	0.0949	0.1013
Platinum	0.0335	0.0355
Glass	0.1770	0.1900

It is difficult to determine whether the increased specific heat observed in solids and liquids at high temperatures is owing to the accumulation of heat within them, or to their dilatation. It is ascribed in general to the latter, and I believe correctly; because the expansion and contraction of gases by change of pressure, without the aid of heat, is attended with corresponding changes of specific heat.

7. Change of specific heat always occasions a change of temperature. Increase in the former is attended by diminution of the latter; and decrease in the former by increase of the latter. Thus when air, confined within a flaccid bladder, is suddenly dilated by means of the air-pump, a thermometer placed in it will indicate the production of cold. On the contrary, when air is compressed, the corresponding diminution of its specific heat gives rise to increase of temperature; nay, so much heat is evolved when the compression is *sudden* and forcible, that tinder may be kindled by it. The explanation of these facts is obvious. In the first case, a quantity of heat becomes insensible, which was previously in a sensible state; in the second, heat is evolved, which was previously latent.

8. A curious relation between the specific heat of some elementary substances and their atomic weight was discovered by Dulong and Petit; namely, that the product of the specific heat of each element by the weight of its atom is a constant quantity. This relation, if general, would be of great interest, as leading directly to the inference that the atoms of elementary substances have the same specific heat, and enabling chemists to calculate either the specific heat of elements from their atomic weight, or conversely their atomic weight from their specific heat. (An. de Ch. et de Ph. x. 403.) The relation above alluded to was exemplified by Dulong and Petit by a table similar to the subjoined.

	Specific Heat.		Relative Weights of atoms.		Product of the sp. heat of each element by the weight of its atom.
Lead	0.0293	×	103.6	=	3.0354
Tin	0.0514	×	57.9	=	2.9760
Zinc	0.0927	×	32.3	=	2.9942
Tellurium	0.0912	×	32.3	=	2.9457
Copper	0.0949	×	31.6	=	2.9988
Nickel	0.1035	×	29.5	=	3.0532
Iron	0.1100	×	28	=	3.0800
Sulphur	0.1880	×	16.1	=	3.0268
Platinum	0.0335	×	98.8	=	3.3098
Bismuth	0.0288	×	71	=	2.0448
Cobalt	0.1498	×	29.5	=	4.4191
Mercury	0.0330	×	202	=	6.6660
Silver	0.0557	×	108	=	6.0156
Gold	0.0298	×	199.2	=	5.9361*

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* Professor A. D. Bache, of the University of Pennsylvania, pointed out in 1829, that the coincidences between the specific heats of the atoms of

It will be observed, on inspecting the last column of the table, that the product of the specific heat into the atomic weight is very nearly 3 for the first eight substances. Platinum deviates visibly from the law, and bismuth and cobalt strikingly. The three last metals would nearly coincide with the law, were their respective atomic weight estimated at half the number given in the table. It is singular that the tabular view originally framed by Dulong and Petit exhibited a more perfect coincidence than appears in my table, and that the difference arises from the substitution of the atomic weights now used for the less correct ones employed by them. This circumstance is so far unfavourable to the notion of a law; but still the cases which do coincide appear too numerous to be the result of chance. Dr. Dalton, in his Chemical Philosophy (ii. 293,) contends that the law cannot be true; since, as Dulong and Petit have shown, the specific heat of a substance is not constant, but varies both from a change of form, and even with variation of temperature without change of form. To the latter part of the criticism, Dulong and Petit are certainly exposed; but they have anticipated the former by remarking, that the law is not affected by change of form, provided the substances compared are taken in the same state. Future observation must decide on the validity of this position.

LIQUEFACTION.

All bodies hitherto known, are either solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together, that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion, that the particles move on each other freely, a liquid is formed. And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but would, unless restrained by external pressure, separate from one another to an almost indefinite extent, an aëriform substance will be produced.

Now the property of repulsion is manifestly owing to heat; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure: that is, by heat sufficiently intense every solid may be converted into a fluid, and every fluid into vapour. This inference is so far justified by experience, that it may safely be considered as a law. The converse ought also to be true, and, accordingly, several of the gases have already been condensed into liquids by means of pressure, and liquids have been solidified by cold. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points are different for different substances, but uniformly the same, under similar circumstances, in the same body.

The most important circumstance relative to liquefaction is the discovery of Dr. Black, that a large quantity of heat disappears, or becomes insensible to the thermometer, during the process. If a pound of water at 32° be mixed with a pound of water at 172°, the temperature of the mixture will be intermediate between them, or 102°. But if a pound of water at 172° be

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bodies is far less striking when the corrected atomic weights are employed, than they appear to be in Dulong and Petit's table, in which the old atomic numbers are used. Dr. Turner here gives a new table, as a substitute for Dulong and Petit's, adopting the atomic weights according to the latest determinations, and confirms Professor Bache's view. A number of errors in the atomic weights and calculations of Dr. Turner's table have been corrected. See Prof. Bache's paper in the Jour. of the Acad. of Nat. Sciences of Philadelphia, for Jan. 1829.—*Ed.*

added to a pound of ice at 32°, the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand, not at 102°, but at 32°. In this experiment, the pound of hot water, which was originally at 172°, actually loses 140 degrees of heat, all of which enters into the ice, and causes its liquefaction, but without affecting its temperature; whence it follows that a quantity of heat becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water by 140 degrees of Fahrenheit. This explains the well known fact, on which the graduation of the thermometer depends,—that the temperature of melting ice or snow never exceeds 32° F. All the heat which is added becomes insensible, till the liquefaction is complete.

The loss of sensible heat which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *heat of fluidity*. The actual quantity of heat required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material may be heated by the heat of fluidity which is proper to it.

	Heat of Fluidity.		Heat of Fluidity.
Sulphur	143.68° F.	Zinc	493° F.
Spermaceti	145°	Tin	500°
Lead	162°	Bismuth	550°
Beeswax	175°		

As so much heat disappears during liquefaction, it follows that heat must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing remains at 32°, though exposed to an atmosphere in which the thermometer is at zero. In order that the water under such circumstances should preserve its temperature, it is necessary that heat should be supplied as fast as it is abstracted; and it is obvious that the only source of supply is the heat of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21° without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so its temperature rises to 32°. (Sir C. Blagden in Phil. Trans. 1788.)

The explanation which Dr. Black gave of these phenomena constitutes what is called his *doctrine* of *latent heat*, which was partially explained on a former occasion. (Page 29.) He conceived that heat in causing fluidity loses its property of acting on the thermometer in consequence of combining chemically with the solid substance, and that liquefaction results, because the compound so formed does not possess that degree of cohesive attraction on which solidity depends. When a liquid is cooled to a certain point, it parts with its heat of fluidity, heat is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Dr. Black to the conversion of liquids into vapours, a change during which a large quantity of heat disappears.

A different explanation of these phenomena was proposed by Dr. Irvine. Observing that a solid has a smaller specific heat than the same substance when in a liquid state, he argued that this circumstance alone accounts for heat becoming insensible during liquefaction. For since the specific heat of ice and water, or in other words, the quantity of heat required to raise their temperature by the same number of degrees, was found to be as 9 to 10, Dr. Irvine inferred that ice must contain one-tenth less heat than water of the same temperature; and that as this difference must be supplied to the ice when it is converted into water, the change must necessarily be accompanied with the disappearance of heat. Dr. Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the heat which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Dr. Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of heat which accompanies liquefaction, but does not explain why the body becomes liquid; whereas the hypothesis of Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Dr. Irvine argued on the belief that a liquid has in every case a greater specific heat than when in the solid state; and though this point has not been demonstrated in a manner entirely decisive, yet from the experiments hitherto made, it appears that liquids in general have a greater specific heat than solids, and that, therefore, Irvine's assumption is probably correct. In like manner he believed vapours to have a greater specific heat than the liquids that yield them, and his opinion was supported by the experiments of Crawford on the specific heat of water and watery vapour. But no reliance whatever can be placed on the researches of Crawford on this subject; not only because his result is so different from that obtained by Delaroche and Bérard, but because all his other experiments on the specific heat of elastic fluids are decidedly erroneous. (Page 32.) Indeed from the fact of most gases having a smaller specific heat than liquids, it is probable that the specific heat of elastic fluids in general is inferior to that of the liquids from which they are derived.* The disappearance of heat during vaporization is, therefore, not explicable on the views of Irvine; it is necessary to employ the theory of Dr. Black to account for that change, and, therefore, the same doctrine should be applied to the analogous phenomenon of liquefaction.

In speculating on the cause of the specific heat of bodies, at page 29, I had recourse to the doctrine of latent or combined heat. Black restricted the use of this hypothesis to explain the phenomena of liquefaction and vaporization; but I apprehend it may be applied without impropriety to all cases where heat passes from a sensible to an insensible state. That this may happen, when heat enters a body, without change of form, is easily demonstrated. Thus, in order to raise an equal weight of water and mercury by the same number of degrees, it is necessary to add 23 times as much heat to the water as to the mercury; a fact which proves that a quantity of heat becomes insensible to the thermometer when the temperature of water is raised by one degree, just as happens when ice is converted into water, or water into vapour.† The phenomena are in this point of view identical; and, therefore, the same mode of reasoning by which one of them is explained, may be employed to account for the other.

The loss of sensible heat in liquefaction is the basis of many artificial processes for producing cold. All of them are conducted on the principle of liquefying solid substances without the aid of heat. For, the heat of fluidity being then derived chiefly from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of heat which disappears, and this again is dependent on the quantity of solid matter liquefied, and on the rapidity of liquefaction.

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt; so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water; that is, a thermometer placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. The crystallized chloride of calcium proposed by Lowitz, is by far the most convenient in practice. It may be made by dissolving marble in muriatic acid, and concentrating the solution by evaporation, *till*, upon letting a drop of it fall upon a cold saucer, it becomes a solid mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must be preserved in well-stopped vessels. The following table, from Mr. Walker's paper in the Philosophical Transactions for 1801, contains the best proportions for producing intense cold.

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* See note, page 34, relating to this point.—*Ed.*

† See note, page 30, where this view of the subject is controverted.—*Ed.*

FRIGORIFIC MIXTURES WITH SNOW.*

MIXTURES.	Parts by weight.	Thermometer sinks		Degree of Cold produced.
Sea-salt . . . . Snow	1 2	from any temperature	to —5°	
Sea-salt . . . . Muriate of ammonia . Snow	2 1 5		to —12°	
Sea-salt . . . . . Muriate of ammonia . Nitrate of potassa . . Snow	10 5 5 24		to —18°	
Sea-salt . . . . Nitrate of ammonia . . Snow	5 5 12		to —25°	
Diluted sulphuric acid† . Snow	2 3		from +32° to —23°	55 degrees.
Concentrated muriatic acid Snow	5 8		from +32° to —27°	59
Concentrated nitrous acid Snow	4 7		from +32° to —30°	62
Chloride of calcium . Snow	5 4		from +32° to —40°	72
Crystallized chloride of calcium . . . Snow	3 2		from +32° to —50°	82
Fused potassa . . . . Snow	4 3		from +32° to —51°	83

But freezing mixtures may be made by the rapid solution of salts, without the use of snow or ice; and the following table, taken from Walker's Essay in the *Philosophical* Transactions for 1795, includes the most important of them. The salts must be finely powdered and dry.

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* The snow should be freshly fallen, dry, and uncompressed. If snow cannot be had, finely powdered ice may be substituted for it.

† Made of strong acid, diluted with half its weight of snow or distilled water.

MIXTURES.	Parts by Weight.	Temperature falls	Degree of Cold produced.
Muriate of ammonia Nitrate of potassa Water	5 5 16	from +50° to +10°	40 degrees.
Muriate of ammonia Nitrate of potassa Sulphate of soda Water	5 5 8 16	from +50° to +4°	46
Nitrate of ammonia Water	1 1	from +50° to +4°	46
Nitrate of ammonia Carbonate of soda Water	1 1 1	from +50° to —7°	57
Sulphate of soda Diluted nitrous acid*	3 2	from +50° to —3°	53
Sulphate of soda Muriate of ammonia Nitrate of potassa Diluted nitrous acid	6 4 2 4	from +50° to —10°	60
Sulphate of soda Nitrate of ammonia Diluted nitrous acid	6 5 4	from +50° to —14°	64
Phosphate of soda Diluted nitrous acid	9 4	from +50° to —12°	62
Phosphate of soda Nitrate of ammonia Diluted nitrous acid	9 6 4	from +50° to —21°	71
Sulphate of soda Muriatic acid	8 5	from +50° to 0°	50
Sulphate of soda Diluted sulphuric acid†	5 4	from +50° to +3°	47

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold might be thus produced; but it is found that when the difference between the mixture and the air becomes very great, the communication of heat from one to the other becomes so rapid, as to put a limit to the reduction. The greatest cold produced by Mr. Walker did not exceed 100 degrees below the zero of Fahrenheit.

Though it is unlikely that we shall ever succeed in depriving any substance of all its heat, it is presumed that bodies do contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount. The mode of conducting such a calculation may be shown by the process of Dr. Irvine. That ingenious chemist proceeded on the assumption, that the actual quantity of heat in bodies is proportional to their specific heat, and that the specific heat remains the same at all temperatures, provided no change of form takes place. Thus, as the specific heat of ice is to that of water as 9 to 10, it follows, according to the hypothesis, that ice contains 1-10th less heat than water, at the same temperature. Now Dr. Black ascertained that this tenth, which is the heat of fluidity, is equal to 140 degrees; whence it was inferred that water at 32° contains 10 times 140 or 1400 degrees of heat.

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* Composed of fuming nitrous acid two parts in weight, and one of water; the mixture being allowed to cool before being used.

† Composed of equal weights of strong acid and water, being allowed to cool before use.

To be satisfied that such calculations cannot be trusted, it is sufficient to know, that the estimates made by different chemists respecting the absolute quantity of heat in water vary from 900 to nearly 8000 degrees.* Besides, did even the estimates agree with each other, the principle of the calculation would still be unsatisfactory; for, in the first place, there is no proof that the quantity of heat in bodies is in the ratio of their specific heats; and, secondly, the assumption that the specific heat of a body is the same at all temperatures, so long as it does not experience a change of form, has been proved to be erroneous by the experiments of Dulong and Petit.

VAPORIZATION.

Aëriform substances are commonly divided into vapours and gases. The character of the former is, that they may be readily converted into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a moderate diminution of that temperature, without change of pressure. Gases, on the contrary, retain their elastic state more obstinately; they are always gaseous at common temperatures, and, with one or two exceptions, cannot be made to change their form, unless by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids. The only difference between gases and vapours is in the relative forces with which they resist condensation.

Heat appears to be the cause of vaporization, as well as of liquefaction, and it is a general opinion that a sufficiently intense heat would convert every liquid and solid into vapour. A considerable number of bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be *fixed* in the fire: those which, under the same circumstances, are converted into vapour, are called *volatile*.

The disposition of various substances to yield vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Liquids are, in general, more easily vaporized than solids, as would be expected from the weaker cohesion of the former. Some solids, such as arsenic and sal ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

Vapours occupy more space than the substances from which they were produced. According to the experiments of Gay-Lussac, water, at its point of greatest density, in passing into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at a temperature of 212° F. and under a pressure of 29.92 inches of mercury. This shows that vapours differ in density. Watery vapour is lighter than air at the same temperature and pressure, in the proportion of 1000 to 1604; or the density of air being 1000, that of watery vapour is 625. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy. As alcohol boils at a lower temperature than water, and ether than alcohol, it was conceived that the density of vapours might be in the direct ratio of the volatility of the liquids which produced them. But Gay-Lussac has shown that this law does not hold generally; since bisulphuret of carbon boils at a higher temperature than ether, and nevertheless it yields a heavier vapour.

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* Dalton's New System of Chemical Philosophy.

The dilatation of vapours by heat was found by Gay-Lussac to follow the same law as gases, that is, for every degree of Fahrenheit, they increase by $\frac{1}{480}$th of the volume they occupied at 32°. But the law does not hold unless the quantity of vapour continue the same. If the increase of temperature cause a fresh portion of vapour to rise, then the expansion will be greater than $\frac{1}{480}$th for each degree; because the heat not only dilates the vapour previously existing to the same extent as if it were a real gas, but augments its bulk by adding a fresh quantity of vapour. The contraction of a vapour on cooling will likewise deviate from the above law, whenever the cold converts any of it into a liquid; an effect which must happen, if the space had originally contained its maximum of vapour. The circumstances just explained should be held in view, whenever the influence of heat over the bulk of vapours is estimated by calculation. The formula of page 21, when applied to vapours, often leads to a result which would be correct for any gas, but which may be untrue in the case of vapour, by reason of its light condensibility. Thus 100 measures of steam at 212°, and when the barometer is at 30 inches, would *theoretically* occupy nearly 73 measures at 32°, and at the same pressure; but this estimate is *practically* untrue, because under the conditions specified water cannot exist in the state of vapour. The calculated result, being deduced from correct principles, is sometimes employed in effecting other calculations.

The volume of vapour varies under varying pressure according to the same law as that of gases, provided always that the gaseous state is preserved. This law, discovered by Boyle and Mariotte, is more fully explained in the section on atmospheric air, and merely expresses the fact that the volume of gaseous substances at a constant temperature is inversely as the pressure to which they are subject. If 100 measures of steam at 212°, and under the atmospheric pressure, be exposed to a pressure of two atmospheres, the vapour will be entirely condensed, affording an instance of failure in the law in consequence of the gaseous state being entirely destroyed; but if the pressure be halved instead of doubled, the 100 measures retaining the gaseous form, and hence acting as a gas, will expand to 200 measures. In fact, if v be the volume corresponding to any pressure p, expressed in inches of mercury, we shall have $\frac{v}{100}=\frac{30}{p}$; and hence $v=100.\frac{30}{p}$. This formula gives the change of volume due to a change of pressure from 30 to p, the temperature being supposed at 212° in both cases. To render the preceding paragraph intelligible to the young student, it should be mentioned that pressure, in reference to the volume of gaseous matter, is usually expressed by the length of a column of mercury: a mercurial column, 30 inches in length, presses on a given surface with the same force as the atmosphere in its ordinary state; and hence a 60-inch column is equal to two atmospheres, 15 inches to half an atmosphere, and one inch to 1-30th of the atmospheric pressure.

Vaporization is conveniently studied under two heads,—*Ebullition* and *Evaporation*. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid; in the second, it passes off quietly and insensibly.

Ebullition.—The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the *boiling point*. The heat requisite for this effect varies with the nature of the liquid. Thus, sulphuric ether boils at 96° F., alcohol at 176°, and pure water at 212°; while oil of turpentine must be raised to 316°, and mercury to 662°, before either exhibits marks of ebullition. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus Gay-Lussac observed that pure water boils precisely at 212° in a metallic vessel, and at 214° in one of glass, owing apparently to its adhering to glass more powerfully than to a metal. It is likewise affected by the presence of foreign particles. The same accurate experimenter found, that when a few iron filings are thrown into water, boiling in a glass vessel, its temperature quickly falls from 214° to 212°, and remains stationary at the latter point. But the circumstance which has the greatest influence over the boiling point of fluids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface. Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact, they cannot enter into ebullition at all, till their particles have acquired such elastic force as enables them to overcome the pressure upon their surfaces; that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, when the barometer stands at 30 inches, and then only does water boil at 212° F. If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water, and of every other liquid, will be lower than usual; or if the barometer rise above 30 inches, the temperature of ebullition will be proportionally increased. This is the reason why water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution. The ratio between the depression of the boiling point and the diminution of the atmospheric pressure is so exact, that it has been proposed as a method for determining the height of mountains. An elevation of 530 feet makes a diminution of one degree of Fahrenheit. (Mr. Wollaston in Phil. Trans. for 1817.)

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. The late Professor Robison found that liquids boil *in vacuo* at a temperature 140 degrees lower than in the open air. (Black's Lectures, p. 151.) Thus water boils *in vacuo* at 72°, alcohol at 36°, and ether at —44° F. This proves that a liquid is not necessarily hot, because it boils. The heat of the hand is sufficient to make water boil in a vacuum, as is exemplified by the common pulse-glass; and ether, under the same circumstances, will enter into ebullition, though its temperature be low enough for freezing mercury.

Water cannot be heated under common circumstances beyond 212°; because it then acquires such expansive force as enables it to overcome the atmospheric pressure, and fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's digester. In this apparatus, on the application of heat, a large quantity of vapour collects above the water, and checks ebullition by the pressure which it exerts upon the surface of the liquid. There is no limit to the degree to which water may thus be heated, provided the vessel is strong enough to confine the vapour; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

In estimating the power of steam it should be remembered that vapour, if separated from the liquid which produced it, does not possess greater elasticity than an equal quantity of air. If, for example, the digester were full of steam at 212°, no water in the liquid state being present, it might be heated to any degree, even to redness, without danger of bursting. But if water be present, then each addition of heat causes a fresh portion of steam to rise, which adds its own elastic force to that of the vapour previously existing; and, in consequence, an excessive pressure is soon exerted against the inside of the vessel. Professor Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244°, and to three at 270° F. The results of Mr. Southern's experiments, given in the same volume, fix upon 250·3° as the temperature at which steam has the force of two atmospheres, on 293.4° for four, and 343·6° for eight atmospheres.

This subject has been lately examined by a commission appointed by the Parisian Academy of Sciences, and Dulong and Arago took a leading part in the inquiry. The results, which are given in the following table, were obtained by experiment up to a pressure of 25 atmospheres, and at higher pressures by calculation. (Brande's Journal, N. S. vii. 191.)

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
1	212°	13	380.66°
1½	233.96	14	386.94
2	250.52	15	392.86
2½	263.84	16	398.48
3	275.18	17	403.82
3½	285.08	18	408.92
4	293.72	19	413.78
4½	300.28	20	418·46
5	307.5	21	422.96
5½	314.24	22	427.28
6	320.36	23	431.42
6½	326.26	24	435.56
7	331.70	25	439.34
7½	336.86	30	457.16
8	341.78	35	472.73
9	350.78	40	486.59
10	358.88	45	491.14
11	366.85	50	510.60
12	374.00		

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by heat, and its ready conversion into water by cold. The effect of both these properties is well shown by a little instrument devised by Dr. Wollaston. It consists of a cylindrical glass tube, six inches long, nearly an inch wide, and blown out into a spherical enlargement at one end. A piston is accurately fitted to the cylinder, so as to move up and down the tube with freedom. When the piston is at the bottom of the tube, it is forced up by causing a portion of water, previously placed in the ball, to boil by means of a spirit-lamp. On dipping the ball into cold water, the steam which occupies the cylinder is suddenly condensed, and the piston forced down by the pressure of the air above it. By the alternate application of heat and cold, the same movements are reproduced, and may be repeated for any length of time.

The moving power of the steam-engine is the same as in this apparatus. The only essential difference between them is in the mode of condensing the steam. In a steam-engine, the steam is condensed in a separate vessel, called the *condenser*, where there is a regular supply of cold water for the purpose. By this contrivance, which constitutes the great improvement of Watt, the temperature of the cylinder never falls below 212°.

The formation of vapour is attended, like liquefaction, with loss of sensible heat. This is proved by the well-known fact that the temperature of steam is precisely the same as that of the boiling water from which it rises; so that all the heat which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either in the slightest degree, provided the latter is permitted to escape with freedom. The heat which then becomes latent, to use the language of Black, is again set free when the vapour is condensed into water. The exact quantity of heat rendered insensible by vaporization, may, therefore, be ascertained by condensing the vapour in cold water, and observing the rise of temperature which ensues. From the experiments of Black and Watt, conducted on this principle, it appears that steam of 212°, in being condensed into water of 212°, gives out as much heat as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr. Ure, whose results are contained in the following table. (Phil. Trans. for 1818.)

	Latent heat.
Vapour of water at its boiling point	967°
Alcohol	442
Ether	302·379
Petroleum	177·87
Oil of turpentine	177·87
Nitric acid	531·99
Liquid ammonia	837·28
Vinegar	875

The disappearance of heat that accompanies vaporization was explained by Black and Irvine, in the way already mentioned under the head of liquefaction; and as the objections to the views of the latter ingenious chemist were then stated, it is unnecessary to mention them on the present occasion.

The variation of volume and elasticity in vapours is attended, as in gases, with a change of specific heat and a consequent variation of temperature. (Page 35.) Thus when steam, highly heated and compressed in a strong boiler, is permitted to escape by a large aperture, the sudden expansion is attended with a great loss of sensible heat: its temperature instantly sinks so much, that the hand may be held in the current of vapour without inconvenience. The same principle accounts for the fact, first ascertained by Watt, that distillation at a low temperature is not attended with any saving of fuel. For when water boils at a low temperature in a vacuum, the vapour is in a highly expanded state, and contains more insensible heat than steam of greater density. From some experiments by Mr. Sharpe in the Manchester Memoirs, and also by Clement and Desormes, (Thenard's Chemistry, i. 79, 5th Ed.) it appears that the sum of the sensible and insensible heat contained in equal weights of steam is exactly the same at all temperatures. Thus, steam at 212°, when condensed and reduced to 32°, gives out 950 degrees of insensible and 180 of sensible heat, the sum of which is 1130. The same weight of steam at 250°, on being condensed and cooled to 32°, gives out likewise 1130 degrees, of which 218 are sensible and 912 insensible heat; whereas at 100° its sensible heat is only 68°, and insensible 1062°, forming the constant sum of 1130. The same is found by Despretz to be true of various other vapours, such as that of alcohol, ether, and turpentine.

Evaporation. Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation occurs at common temperatures. This fact may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most liquids, if not all of them, are susceptible of this gradual dissipation; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some liquids than in others, and it is always found that those liquids, the boiling point of which is lowest, evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates with still greater rapidity.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of liquids, and, therefore, *cæteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered appreciable diminution.

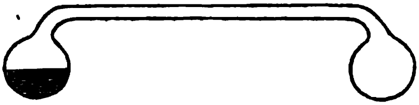
3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contain much vapour, even though the air be very warm.

4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air be removed from the surface of the water as soon as it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

5. Pressure on the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air-pump, when vapour rises so abundantly as to produce ebullition.

As a large quantity of heat passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. The fact may readily be proved by letting a few drops of ether evaporate from the hand, when a strong sensation of cold will be excited; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation, it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so, is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity. But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it is formed. Such is the principle of Leslie's method for freezing water by its own evaporation.*

The action of the cryophorus, an ingenious contrivance of the late Dr. Wollaston, depends on the same principle. It consists of two glass balls, perfectly free from air, and joined together by a tube as here represented.



One of the balls contains a portion of distilled water, while the other parts of the instrument, which appear empty, are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon its surface. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.

Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump, is so intense as, under favourable circumstances, to freeze mercury.*

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* See art. Cold, in the Supplement to the Encyclopædia Britannica.

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally *in vacuo* as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it, is by removing the air altogether. The experiments of Dalton prove that heat is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour, which can exist in any given space, is dependent solely upon the temperature. If, for instance, a little water be put into a dry glass flask, a quantity of vapour will be formed proportionate to the temperature. If a thermometer placed in it stands at 32°, the flask will contain a very small quantity of vapour. At 40°, more vapour will exist in it; at 50° it will contain still more; and at 60°, the quantity will be still further augmented. If, when the thermometer is at 60°, the temperature of the flask be suddenly reduced to 40°, then a certain portion of vapour will be converted into water; the quantity which retains the elastic form being precisely the same as when the temperature was originally at 40°.

It matters not, with regard to these changes, whether the flask is full of air, or altogether empty; for in either case, it will eventually contain the same quantity of vapour, when the thermometer is at the same height. The only effect of a difference in this respect, is in the rapidity of evaporation. The flask, if previously empty, acquires its full complement of vapour, or, in common language, becomes saturated with it, in an instant; whereas the presence of air affords a mechanical impediment to its passage from one part of the flask to another, and, therefore, an appreciable time elapses before the whole space is saturated.

Dalton found that the tension or elasticity of vapour is always the same, however much the pressure may vary, so long as the temperature remains constant, and there is liquid enough present to preserve the state of saturation proper to the temperature. If, for example, in a flaccid bladder containing a little water, the pressure on its surface be diminished, the vapour in the interior will expand proportionally, and consequently for the moment will diminish in elasticity, because the tension of gaseous substances at a constant temperature diminishes in the same ratio as the volume increases, or, in other words, the elasticity varies inversely as the volume; but the vapour in the bladder will speedily recover its original tension, since the water will yield an additional quantity of vapour proportional to the increase of space. Again, if the pressure on the bladder be increased so as to diminish its capacity, the temperature remaining constant, the tension of the confined vapour will *still* continue unchanged, because a portion of it will be condensed proportional to the diminution of space; so that, in fact, the remaining space contains the very same quantity of vapour as it did originally. The same law holds good, whether the vapour is pure, or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below 212° was carefully examined by Dalton, (Manchester Memoirs, vol. v.); and his results, together with those since published by Dr. Ure, in the Philosophical Transactions for 1818, are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures. But Dalton did not confine his researches to water; he extended them to the vapour of various liquids, such as ether, alcohol, ammonia, and solution of chloride of calcium, and he inferred from them the following law:—that the force of vapour from all liquids is the same, at equal distances above or below the several temperatures at which they boil in the open air. Subsequent observations by Dr. Ure, Despretz, and others, have proved that the law is far from universal, and that it fails remarkably at temperatures distant from the point of ebullition: it has, indeed been abandoned by Dalton himself.

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* See a paper by the late Dr. Marcet, in Nicholson's Journal, vol. xxxiv.

A knowledge of the influence of heat and pressure over the volume of gaseous matter is elegantly employed in calculating the density of vapour; but before giving the mode of making the calculation, it will be useful to explain what is meant by *density*. This term is generally used synonymously with *specific gravity*, and indicates the compactness of a substance, or the quantity of ponderable matter contained in a body compared with the space which it occupies. The density of a substance is found by dividing its weight by its volume. Thus, if d, w, v, represent the density, weight, and volume of aqueous vapour, and d', w', v', the density, weight, and volume of air, then $d = \frac{w}{v}$, and $d' = \frac{w'}{v'}$. Hence, comparing these densities, $d : d' :: \frac{w}{v} : \frac{w'}{v'}$; if the volumes are equal, then $d : d' :: w : w'$; and if the weights are equal, $d : d' :: \frac{1}{v} : \frac{1}{v'}$. Consequently, the density of substances which have an equal volume, is directly as their weight; and when the weights are equal, the densities are inversely as the volumes. Accordingly, if we weigh an equal volume of any number of substances, temperature and pressure being the same in all, the density of each respectively will be represented by its weight. Thus, Gay-Lussac ascertained that if a certain volume of air at 212° and 30 Bar. weigh 1000 grains, an equal volume of aqueous vapour, at the same temperature and pressure, will weigh 625 grains; and, therefore, the density of steam is 625 compared to that of air as 1000. Atmospheric air is universally taken as a term of comparison for the density of gaseous substances, and pure water for that of liquids and solids.

As gases expand and contract, from varying temperature and pressure, according to the same laws, it follows that the densities found at any one temperature and pressure are constant for all others. Thus if air is twice as heavy as an equal volume of a certain gas, both being weighed at 32° and 30 Bar., the same ratio will be found at 32° and 15 Bar., and at 212° and 30 Bar. The same remark applies to vapours, except when they suffer condensation. For example, the density of air and steam, both being weighed at 212° and 30 Bar., is expressed by 1000 and 625: the same ratio is preserved at 212° and at any other pressure less than 30 Bar., because in that case the vapour will expand like air; but if the pressure be increased, or the temperature diminished, condensation occurs, and the density of the vapour falls below 625. Hence it happens that the density of vapours varies with the temperature, as is exemplified by the following table, showing the greatest density of aqueous vapour at the temperatures stated, the corresponding elasticities agreeably to Dalton's table, and the weight of 100 cubic inches of the vapour.

Temp.	Elasticity in inches of mercury.	Density.	Weight of 100 cubic inches.
32° F.	0.2	5.7292	0.13716 grains.
50°	0.375	10.3539	0.2478
60°	0.524	14·18306	0.3394
100°	1.860	46.6697	1.117
150°	7.42	170.61	4.084
212°	30	625	14.96

In calculating these densities, it is assumed that the laws of gaseous expansion by varying heat and pressure are true,—that the density of steam at

212° F. and 30 Bar. is 625, compared to air at the same temperature and pressure as 1000,—and that 100 cubic inches of air at 212° and 30 Bar. weigh 23.94 grains. The formula for the calculation is thus deduced:—If d is the density of aqueous vapour at any pressure p, then since both the density and elasticity of gaseous substances vary inversely as their volume, the density and elasticity are proportional to each other; so that $d : 625 :: p : 30$, and hence $d=625.\frac{p}{30}$. This gives the density of aqueous vapour at 212°, and with an elasticity equal to p. In this state the vapour is rarefied, and will admit of being cooled down to a certain point, but not lower, say to t degrees above 32°, without condensation; and when it has reached that point, its density has acquired a *maximum*. Its elasticity remains unchanged, because the loss of tension due to loss of heat is compensated for by diminution of volume. Its density has increased exactly in the same ratio as its volume has diminished, and, therefore, the formula of page 21 inverted will give the increased density owing to decrease of temperature. Hence we shall have $d=625\cdot\frac{p}{30}\frac{480+180}{480+t}$. For example, if we wish to calculate the greatest density of aqueous vapour at 100° F., then $t=68$, and the elasticity of that vapour by Dalton's table is 1.86. Inserting these values of t and p in the preceding formula, we shall find $d=625.\cdot\frac{1.86}{30}\cdot\frac{660}{548}=46.6697$.

It admits of inquiry whether liquids of weak volatility, such as mercury and oil of vitriol, give off any vapour at common temperatures. An opinion has prevailed, that evaporation not only takes place from the surface of these and *similar* liquids at all times, but that vapour of exceedingly weak tension *is emitted* at common temperatures from all substances however fixed in the fire, even from the earths and metals, when they are either in a vacuum, or surrounded by gaseous matter. It has accordingly been supposed, that the atmosphere contains diffused through it minute quantities of the vapours of all the bodies with which it is in contact; and this idea has been made the basis of a theory of the origin of meteorites. But this doctrine has been successfully combated by Mr. Faraday, in his essay On the Existence of a Limit to Vaporization, published in the Philosophical Transactions for 1826. The argument employed by Mr. Faraday is founded on the principle by which the late Dr. Wollaston accounted for the limited extent of the atmosphere. Since the volume of gaseous substances is dependent on the pressure to which they are subject, the air in the higher regions of the atmosphere must be much more rare than that in the lower, because the former sustains the pressure of a shorter atmospheric column than the latter; so that in ascending upwards from the earth, each successive stratum of air, being less compressed than the foregoing, is likewise more attenuated. Now it is found experimentally, that the elasticity or tension of any gaseous matter *diminishes* in the same ratio as its volume increases; and, accordingly, whenever the tenuity of a portion of air, owing to its distance from the earth's surface, or any other cause, is exceedingly great, its tension is exceedingly small. Reasoning on this principle, Wollaston conceived that at a certain altitude, probably at a distance of 40 or 50 miles from the surface of the earth, the rarefaction and consequent loss of elastic force is so extreme, that the mere gravity of the particles becomes equal to their elasticity and thus puts a limit to their separation.

What Wollaston suggested of aërial particles, Mr. Faraday supposes to occur in all substances; and this supposition is perfectly legitimate, because gaseous matter in general is subject to the same law of expansion, and is likewise under the influence of gravity. He infers that every kind of matter ceases to assume the elastic form, whenever the gravitation of its particles is stronger than the elasticity of its vapour. The loss of tension necessary for effecting this object may be accomplished in two ways, either by extreme dilatation, or by cold. For substances of great volatility, such as air and most gases, the former condition is necessary; because the degree of cold which we can command at the earth's surface diminishes their tension in a degree quite insufficient to destroy their elasticity. But the volatility of numerous bodies is so small, that their vapour at common temperatures approximates in rarity to the air at the limits of the atmosphere, and a small degree of cold may suffice for rendering its elasticity a force inferior to its opponent, gravity. In that case, the vapour would be entirely condensed. Mr. Faraday found that mercury, at a temperature varying from 60° to 80°, yields a small quantity of vapour; but in winter no trace of vapour could be detected. Hence it is inferred, that at the former temperature the elasticity of mercurial vapour is slightly superior to the gravity of its particles, and that in cold weather the latter power preponderates, and puts an entire check to the evaporation of mercury. The earths and metals, which are more fixed than mercury, have vapours of such feeble tension, that the highest natural temperature is unable to convert them into vapour. Another force, which co-operates with gravity in overcoming elasticity, is the attraction of aggregation, or the attraction exerted by a solid or liquid on the contiguous particles of the same substance in the gaseous form.—This argument affords very sufficient grounds for believing that the vapours of earthy and metallic substances are never present in the atmosphere; and Mr. Faraday has proved that several chemical agents, kept in a confined space with moisture during four years, did not undergo the slightest evaporation. (Journal of the R. Inst. I.: N. S.)

The presence of vapour has a considerable influence over the bulk of gases; and as chemists generally determine the quantity of gaseous substances by measure, it is important to estimate the increase of volume due to the presence of moisture. The mode by which a vapour acts is obvious. When two gases, which do not act chemically on each other, are intermingled, each retains the elasticity suited to its volume, exactly as if the other gas were absent; so that the elasticity of the mixture is the sum of the elastic forces of its ingredients. The same remark applies to the mixture of gases and vapours. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature; for it is the temperature alone which determines the elasticity of the vapour.

As the elasticity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence gives rise, by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced. Let n be the bulk of dry air or other gas expressed in the degrees of a graduated tube; p the elasticity of the dry air, equal to the atmospheric pressure as measured by a barometer; n' the bulk of the air when saturated with watery vapour, and f the elasticity of that vapour. (Biot's Traité de Phys. i. 303.) Now as the elasticity of a gas for equal temperatures is inversely as its volume, it follows that when the dry air increases in bulk from n to n', its elasticity will diminish in the ratio of n' to n. Hence its elasticity ceases to be $= p$, and is expressed by $\frac{pn}{n'}$: p is then $= \frac{pn}{n'} + f$; that is, the elasticity of the moist air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values: $pn + fn' = pn'$; $pn = pn' - fn'$; and $n = \frac{n'(p-f)}{p}$. One example will suffice for showing the use of this formula. Having 100 measures of air saturated with watery vapour at 60° F., the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n' = 100$; $p = 30$; $f = 0.524$, the tension of watery vapour at 60°, according to Dalton's table. Hence $n = \frac{100 \times (30 - 0.524)}{30} = \frac{100 \times 29.476}{30} = 98.25$, which is the answer required.

The preceding formula is true only when the gas is confined in a space which readily enlarges proportionally to the additional pressure, as when a tube full of air is inverted over mercury. If the gas is contained in a space which does not admit of enlargement, and a drop of water is admitted, the aqueous vapour adds its elastic force f to that of the gas p, causing the pressure against the containing vessel to be equal to $p + f$.

The presence of aqueous vapour in the atmosphere is owing to evaporation. All the accumulations of water upon the surface of the earth are subjected by its means to a natural distillation; the impurities with which they are impregnated remain behind, while the pure vapour ascends into the air, gives rise to a multitude of meteorological phenomena, and after a time descends again upon the earth. As evaporation goes on to a certain extent even at low temperatures, it is probable that the atmosphere is never absolutely free from vapour.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

A great many hygrometers have been invented; but they may all be referred to three principles. The construction of the first kind of hygrometer is founded on the property possessed by some substances of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Almost all bodies have the power of attracting moisture from the air, though in different proportions. A piece of glass or metal weighs sensibly less when carefully dried, than after exposure to a moist atmosphere; though neither of them is dilated, because the water cannot penetrate into their interior. Dilatation from the absorption of moisture appears to depend on a deposition of it within the texture of a body, the particles of which are moderately soft and yielding. The hygrometric property, therefore, belongs chiefly to organic substances, such as wood, the beard of corn, whalebone, hair, and animal membranes. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but, by reason of its elasticity, recovers its original length on drying. The hygrometer of Saussure is made with this material.

The second kind of hygrometer points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times, is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation. The most convenient method of doing this is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Leslie's hygrometer is of this kind.

The third kind of hygrometer is on a principle entirely different from the foregoing. When the air is saturated with vapour, and any colder body is brought into contact with it, deposition of moisture immediately takes place on its surface. This is often seen when a glass of cold spring water is carried into a warm room in summer; and the phenomenon is witnessed during the formation of dew, the moisture appearing on those substances only which are colder than the air. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point.* If the saturation be complete, the least diminution of temperature is attended with the formation of dew; but if the air is dry, a body must be several degrees colder before moisture is deposited on its surface; and indeed the drier the atmosphere, the greater will be the difference between its temperature and the dew-point. Attempts were made to estimate the hygrometric state of the air on this principle by the Florentine Academicians, but the first accurate method was introduced by M. le Roi, and since adopted by Dalton. It consists simply in putting cold water into a glass vessel, the outside of which is carefully dried, and marking the temperature of the liquid at which dew begins to be deposited on the glass. The water when necessary is cooled either by means of ice or a freezing mixture. A convenient form of apparatus is a small cup made of thin silver, nicely gilt on the outside, capable of holding about half an ounce of water, and fitted into a case of turned wood lined with cloth, which serves as a stand for the cup during an observation. The water is cooled by successively adding a few grains of a powder made of equal parts of nitre and sal ammoniac intimately mixed, stirring with the bulb of a small thermometer. As soon as dew is deposited, the temperature is noted; and the first observation is corrected by waiting until the cup and its contents grow warmer, and observing the temperature at which the dew begins to disappear. The last observation is the most trustworthy. This method, when deliberately performed, so that the cup, the solution, and the thermometer, should have time to acquire the same temperature, is susceptible of great precision.

The hygrometer of Professor Daniell, described in his Meteorological Essays, acts on the same principle. It consists of a cryophorus, as described at page 46, but modified somewhat in form, and containing ether instead of water. Within one of its balls is fixed a delicate thermometer, the bulb of which is partially immersed in the ether so as to indicate its temperature, and the other ball is covered with muslin. When the instrument is used, the muslin is moistened with ether, and the cold produced by its evaporation condenses the vapour within the cryophorus, and causes the ether to evaporate rapidly in the other ball. The cold thus generated chills the ether itself and the ball containing it; and in a short time its temperature descends so low, that dew is deposited on the surface of the glass. As soon as this takes place, the temperature is observed by the thermometer.

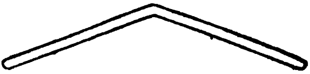
The same object is attained in a still easier way by means of a contrivance described by Mr. Jones of London in the Philos. Trans. for 1826, and soon after in the Edin. Philos. Journal, No. xvii. p. 155, by Dr. Coldstream of Leith. It consists of a delicate mercurial thermometer, the bulb of which is made of thin black glass, and, excepting about a fourth of its surface, is covered with muslin. On moistening the muslin with ether, the temperature of the bulb and mercury falls, and the uncovered portion of the bulb is soon rendered dim by the deposition of moisture. The temperature indicated at that instant by the thermometer is the dew-point. It appears from some remarks by Professor Daniell in the Quarterly Journal of Science, that this hygrometer was originally invented in Germany, so that Mr. Jones and Dr. Coldstream are second inventors. Professor Daniell considers the instrument inaccurate, believing that, as the ether is applied to a part only of the bulb, the mercury within will be cooled unequally; that the portion corresponding to the covered part of the bulb will be colder than the mercury opposite to the exposed part; and, consequently, that the dew-point will appear lower than it ought to be. This objection certainly applies when the muslin is rendered very moist with ether, and the temperature of the bulb is rapidly reduced; but when the cooling is slowly effected, I believe the indications of this hygrometer to be at least as correct as those afforded by the very elegant, yet more costly and less portable, apparatus of Professor Daniell. For facts confirmatory of this opinion the reader may consult an essay in the Edinburgh Journal of Science, No. xiii. p. 36, by Mr. Foggo, junior, of Leith.

It is desirable on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to intense cold; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to chloride of calcium.

CONSTITUTION OF GASES WITH RESPECT TO HEAT.

The experiments of Mr. Faraday, on the liquefaction of gaseous substances, appear to justify the opinion that gases are merely the vapours of extremely volatile liquids. Most of these liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and hence they are always found in the gaseous state. By subjecting them to great pressure, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they resume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. Intense cold is produced at the same time, in consequence of their heat passing from a sensible to an insensible state.

The process for condensing gases (Philos. Trans. for 1823) consists in exposing them to the pressure of their own atmospheres. The materials for producing the gas are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle, as represented by the figure. The gas is generated, if necessary, by the application of heat, and when the pressure becomes sufficiently great, the liquid is formed and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.



The pressure required to liquefy gases is very variable, as will appear from the following table of the results obtained by Mr. Faraday.

Sulphurous acid gas . .	2 atmospheres at	45° F.
Sulphuretted hydrogen gas	17	50°
Carbonic acid gas . .	36	32°
Chlorine gas	4	60°
Nitrous oxide gas . .	50	45°
Cyanogen gas . . .	3.6	45°
Ammoniacal gas . .	6.5	50°
Muriatic acid gas . .	40	50°*

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* The general law in regard to the elasticity or tension of gases is that this property is directly proportional to the compressing force. Oersted, however, has shown, that it does not always hold; for he ascertained that condensable gases, subjected to a pressure approaching to that at which their condensation would take place, undergo a greater diminution of volume than is proportional to the pressure. Berzelius accounts for this fact by supposing that the close proximity of the molecules of a gas, occasioned by great pressure, brings the particles more completely within the sphere of each other's attraction, and thus counteracts the separating power of the caloric, which he conceives to act under unfavourable circumstances, unless the ponderable particles are at a certain distance apart. (Berzelius, Traité de Chimie, i. 83, 86.) These views have a bearing on the experiments of Mr. Faraday cited in the text. *Ed.*

SOURCES OF HEAT.

The sources of heat may be reduced to six. 1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action. All these means of procuring a supply of heat, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting heat is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is sufficient for kindling wood. The axle-tree of carriages has been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Rumford has given an interesting account of the heat excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that heat cannot be a material substance, but is merely a property of matter. Pictet observed that solids alone produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

SECTION II.

LIGHT.

Optics, from ὀπτομαι, *I see*, is the science which treats of light and vision. Of the nature of light two rival theories are entertained. According to some, and this was the theory sanctioned by the great authority of Newton, light is an emanation from luminous bodies, such as the sun, the fixed stars, and incandescent substances; and consists of inconceivably minute particles, which are too subtile to exhibit the common properties of matter, travel in straight lines with immense velocity, and produce the sensation of light by passing into the eye, and striking against the expanded nerve of vision, the *retina*. Others deny to light a separate material existence, and ascribe its effects to the vibrations or undulations of a subtile ethereal medium universally present in nature, the pulses of which, in some way excited by luminous objects, pass through space and transparent bodies, and give rise to vision by impressing the retina, in the same way as pulsations of air impress the nerve of hearing, and produce the sensation of sound. The latter, the *undulatory theory of light*, which was formerly maintained by Descartes, Huygens, and Euler, but subsequently fell into disuse, has of late received powerful support from Sir John Herschel and Professor Airy, who in their analytic researches on polarized light find the phenomena more fully explicable on the undulatory than by the *Newtonian theory*. In this, however, as in some other departments of science, either of two theories serves the purpose of classifying facts and explaining most of the phenomena, the advantage lying sometimes on one side and sometimes on the other. At present, the strongest evidence is in favour of the undulatory theory; but as the views of Newton are still generally used and understood, and readily apply to all the subjects which the design of this work admits of being noticed here, I shall continue to adopt it, referring those who are prepared to study the undulatory theory to Sir J. Herschel's article on light in the *Encyclopedia Metropolitana*, and to the Mathematical Tracts, 2nd edition, of Professor Airy.

Diffusion of Light.—Light is emitted by every visible point of a luminous object, and is equally distributed on all sides, if not intercepted, diverging like radii drawn from the centre to the circumference of a circle. Thus, if a single luminous point were placed in the centre of a hollow sphere, every point of its concavity would be illuminated, and equal areas would receive equal quantities of light. The smallest portion of light which can be separated from contiguous portions, is called a *ray of light*. Each ray, when not interrupted in its course, and while it remains in the same medium, moves in a straight line; as is obvious by the appearance of shadows cast by the side of a house, or of a sun-beam admitted through a small aperture into a dark room. Owing to these modes of distribution, it follows that the quantity of light which falls upon a given surface decreases as the square of its distance from the luminous object increases, the same law which regulates the heating power of a hot body. (Page 9.)

The passage of light is progressive, time being required for its motion from one place to another. By astronomical observations it is found that light travels at the rate of nearly 195,000 miles in a second of time, and would require about eight minutes to pass from the sun to the earth. Owing to this prodigious velocity, the light emitted in the firing of a cannon or a sky-rocket is seen by different spectators at the same instant, whatever may be their respective distances from the rocket, the time required for light to travel 100 or 1000 miles being inappreciable to our senses.

When light falls upon any body, it may, like radiant heat (page 9,) dispose of itself in three different ways, being *reflected*, *refracted*, or *absorbed*. The phenomena connected with the two former modes of distribution I shall proceed to consider in succession; while those of absorbed light will be included under the head of *Decomposition of Light*.

REFLECTION OF LIGHT.

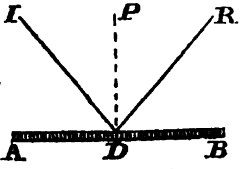
Light, so far as is known, is not reflected by purely gaseous bodies; but it is reflected by air containing floating particles of moisture in the form of clouds, and by all solids and liquids, though in very different degrees. Bright metallic surfaces, such as polished brass and silver, or clean mercury, reflect nearly all the rays which fall upon them; while those which are dull and rough, reflect but few of the rays. The reflection of light, like that of heat, takes place at the surface of bodies, and appears influenced rather by the condition of the surface than by the nature of the reflecting body. The direction of the reflected ray, whatever may be the nature or figure of the reflecting surface, is regulated by these two laws.

I. The incident and reflected ray always lie in the same plane, which plane is perpendicular to the reflecting surface.

II. The incident and reflected ray always form equal angles with the reflecting surface; or, what amounts to the same, the angle of incidence is always equal to the angle of reflection.

Let AB, figure 1, represent a plane mirror, ID the direction of a ray falling on AB at the point D, and DP a line perpendicular to the mirror AB. Then a plane passing through IDP will be perpendicular to AB, and, by the first law, the reflected ray DR will lie *somewhere* in that plane. Also, by the second law, the angle of reflection RDP must be equal to the angle of incidence IDP. Hence, as soon as the direction of the incident ray is given, that of the reflected ray is known also.

Fig. 1.



These laws apply equally to convex and concave mirrors. A circle or any curve may be viewed as a polygon with very short sides circumscribing the curve, as shown in *ab*, fig. 2; and on this principle a tangent *tt'* at any point D of a curve AB, may be taken as identical at the touching point with the curve itself. Similarly, may a plane, tangent to a curved surface, be considered as part of that surface at the point of contact. The action of a curved mirror may hence be referred to that of a number of tangent planes, which will reflect light agreeably to the two laws above mentioned. Thus, let AB, fig. 3, be a convex mirror, being a segment of a sphere, the centre of which is C; let ID, I'D' be parallel rays, incident at D, D'. The dotted lines DP, D'P' will be respectively perpendicular to the tangent at D, D'; the angles of incidence are IDP, I'D'P'; and PDR, P'D'R', the angles of reflection. Parallel rays falling on a convex mirror are obviously scattered or made to diverge.

Fig. 2.

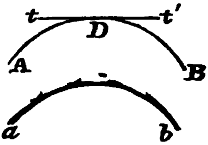
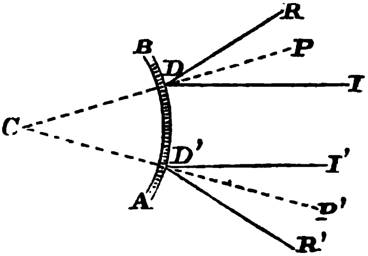
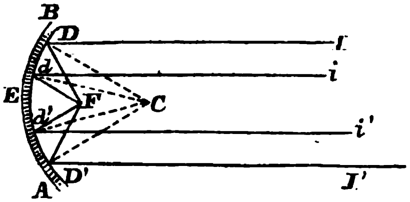


Fig. 3.



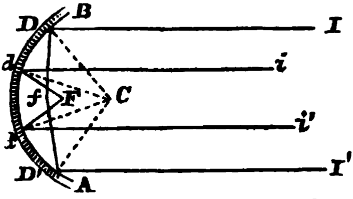
On the same principle must parallel rays falling on a concave spherical mirror, as represented by fig. 4, be so reflected as to converge and meet together at one point F, which is called its *focus for parallel rays*, or its *principal focus*, and is situated midway between the centre C, and the axis of the mirror E. The dotted lines represent the perpendicular to the tangent at the respective points of incidence, D, D' *d*, *d'*. From the same figure it is obvious that the diverging rays emitted by a light placed in the focus of a concave mirror are rendered parallel by reflection. If the light be placed between E and F, then the rays will continue divergent after reflection. On placing the light between F and C, the incident rays, diverging less rapidly than when the light was at F, will converge after reflection, and meet at some point beyond C, which point is more remote from C the nearer the light is to F. When the light is at C, all the rays are reflected back to C; since each ray will then be perpendicular to the tangent at its point of incidence. The student will easily comprehend these statements, if he will but take rule and compass, and draw a few figures for himself.

Fig. 4.



The statement above made, that parallel rays are collected into *one* point by reflection from a concave spherical mirror, is not strictly correct. When the mirror is very flat, being a small segment of a large sphere, the rays meet very nearly in one point; but they are far from doing so when the curvature of the mirror is considerable. This defect of spherical mirrors, which arises from their form, and is termed *spherical aberration*, is exhibited in fig. 5, where the rays *id*, *i'd'*, near the axis, meet at F; whereas the remoter rays ID, I'D', are collected at *f*. The consequence of such aber-

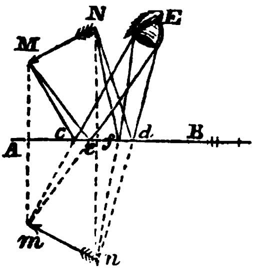
Fig. 5.



ration is a confused image, a defect which is remedied by diminishing curvature, and cutting off by screens the rays most distant from the axis. Parabolic reflectors, when accurately made, are entirely free from this inconvenience.

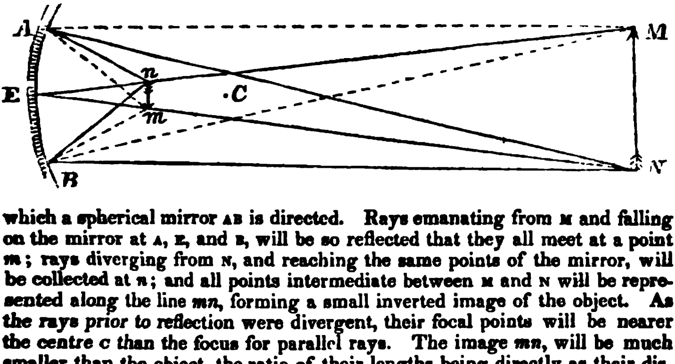
The position in which objects are seen after being reflected will now be easily understood. Let MN, fig. 6, be an arrow placed before a plane mirror AB, E the eye of an observer, MC Me rays emanating from the point of the arrow, and Nf Nd rays proceeding from its shaft. The only reflected rays which reach the eye are those that fall between the points *c* and *d*. Those issuing from any single point, M, continue to diverge at the same rate after as before reflection; and, though they are reflected and enter the eye separately, they are collected together by the refracting power of that organ, and appear to the observer to issue from a point *m*, at which, if continued back, they would intersect. The same is true of rays issuing from N, and from all points intermediate between M and N. By inspecting the figure it will be seen that each part of the image *mn* is at the same distance behind the mirror as the object MN is before it, and that the image and object have the same length; consequences which flow necessarily from the laws of reflection and the known properties of triangles.

Fig. 6.



Again, let the arrow MN, fig. 7, represent a high distant object, towards which a spherical mirror AB is directed. Rays emanating from M and falling on the mirror at A, E, and B, will be so reflected that they all meet at a point *m*; rays diverging from N, and reaching the same points of the mirror, will be collected at *n*; and all points intermediate between M and N will be represented along the line *mn*, forming a small inverted image of the object. As the rays prior to reflection were divergent, their focal points will be nearer the centre C than the focus for parallel rays. The image *mn*, will be much smaller than the object, the ratio of their lengths being directly as their distances from the mirror, a relation which the geometric reader will discover for himself by inspecting the figure: if MN be 1000 feet from the mirror, and *mn* at one foot, the image will be diminished in length 1000 times. Hence, as the size and position of the image can be measured, the distance of the object may be calculated if we know its size; or its size may be inferred from a knowledge of its distance.

Fig. 7.



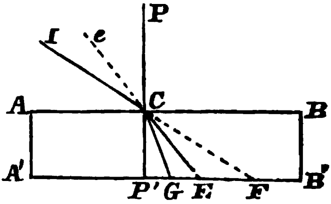
The construction of the simple reflecting telescope depends on the principle just explained. The small size of the image is compensated for, partly by its brightness, since each point is formed by the concentration of many rays, and partly by the advantage of placing the eye close to it. In order to see the image *mn*, the observer may place in the focus a piece of ground-glass or tissue-paper; or, a hole being cut in the mirror at E, the image may be received on a small plane mirror placed in the focus, and be reflected to the observer at E. Instead of using a plane mirror for this purpose, *mn* may be considered as a new *object*, and be reflected by a second smaller concave mirror placed between *mn* and c, and in front of AB; for the converging rays which meet at any point *m* of the image, cross each other at that point, and then diverge exactly as though the place of the image were occupied by a real arrow. The second mirror may be so placed as to magnify the image *mn*; and the second image may be still further enlarged by a convex lens. Compound reflecting telescopes are constructed on this principle.

The arrangement displayed by figure 7 is exactly that of a simple reflecting microscope, provided *mn* be viewed as a small real object, and MN as its magnified inverted image. If *mn* were placed in the principal focus, the reflected rays would be parallel, and hence could not meet to form an image; but if situated rather beyond the principal focus, as in the figure, then the rays converge after reflection, and give an enlarged image of the small object. The ratio of the length of the object and image will, as before, be as their respective distances from the mirror.

REFRACTION OF LIGHT.

Light traverses the same transparent medium, such as air, water, or glass, in a straight line, provided no reflection occurs, and there is no change of density; but when it passes from one medium into another, or from one part of the same medium into another of a different density, a change of direction always ensues at the place of junction of the media, except when the ray is perpendicular to that plane. For instance, let AB A'B', fig. 8, represent a vertical section of a vessel full of water, and PP' the perpendicular to the surface of the water at the point C. Should a ray of light enter the water perpendicularly to its surface, as in the line of PC, it will continue on its course to P' without deviation; but if it descend obliquely, as in the direction of IC, it will suffer a bend at C, and proceed to E, instead of advancing along the dotted line to F. Conversely, were a ray of light to emanate from E and emerge at C, it would not advance to *e*, but take the direction of CI. By comparing the direction of the refracted ray in these two cases in relation to the vertical PP', it will be seen that the ray approaches the perpendicular in entering from air into water, and recedes from it in passing out of water into air. The same remark applies to the passage of light from or into air into or out of solid or liquid media in general.

Fig. 8.



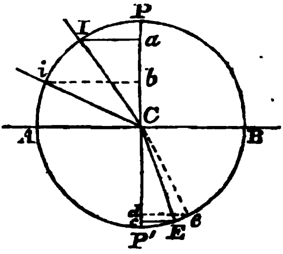
Bodies differ in their power of refracting light. In general, the denser a substance is, the greater is the deviation which it produces. If in fig. 8 sulphuric acid were mixed with the water, the ray IC would be refracted to some point between E and G; and if a solid cake of glass were substituted for that liquid, the refracted ray would be bent down to CG. But this is far from universal:—alcohol, ether, and olive oil, which are lighter than water, have a higher refractive power. Observation has shown it to be a law, to which no exception is yet known, that oils and other highly inflammable bodies, such as hydrogen, diamond, phosphorus, sulphur, amber, olive oil, and camphor, have a refractive power which is from two to seven times greater than that of incombustible substances of equal density. But whatever may be the refractive power of bodies in relation to each other, refraction is always governed by the two following laws, discovered in 1618, by Snell, though usually ascribed to Descartes.

1. The direction of the incident and refracted ray is always in a plane perpendicular to the surface common to the media.

2. The sine of the angle of incidence and the sine of the angle of refraction are in a constant report for the same media.

The first law is similar to the first law of reflection already explained.—(Page 55.) To explain the second law, let ABE, fig. 9, be a vertical section of a refracting medium, PP′ the perpendicular to it, IC a ray of light incident at C, and CE the refracted ray. Then ICP is the *angle of incidence*, and ECP′ the *angle of refraction*. Also from C, as a centre, with any radius CI, and in the plane of the ray ICE, draw a circle; and from the points I and E, where the course of the ray cuts the circle, let fall I*a*, E*c* at right angles to PP′. Then may I*a* be considered the *sine* of the angle of incidence, and E*c* the *sine* of the angle of refraction.

Fig. 9.

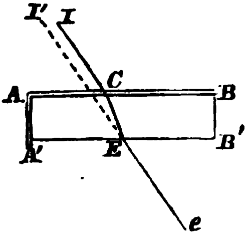


The second law denotes that these lines are for each substance in a constant ratio, whatever may be the direction of the incident ray. In the figure the sine of the angle of refraction is to the sine of the angle of incidence as 1 to 2; and this ratio being once determined, each ray must conform itself to it, so that any angle of incidence being given, the direction of the refracted ray may be foretold. Thus, if *i*C be a second ray incident at C, of which *ib* is the sine of the angle of incidence, the ray will be bent into such a course, that *ed* shall be to *ib* as 1 is to 2. This ratio is nearly that observed in glass made of one part of flint to three of oxide of lead. In common flint-glass the ratio is nearly as 1 to 1.6; in water it is as 1 to 1.336; in oil of cassia as 1 to 1.641; in diamond as 1 to 2.755; in phosphorus as 1 to 2.224; and in melted sulphur as 1 to 2.148. By thus representing the sine of the angle of refraction by 1, the sines of the angle of incidence in all bodies refer to the same unit of comparison, and are, therefore, at once comparable with each other: such numbers are called *indices of refraction*, and indicate the degree of refractive power. For example, the *index of refraction*, for water is 1.336; for flint-glass 1.6; and for diamond 2.755.

By means of Snell's laws of refraction, and with a knowledge of the indices of refraction, the course of a ray of light through any medium may be indicated, whatever may be the nature or figure of that medium, or the direction of the ray. The refracting substance most used in optics is glass, which is ground into different forms, such as prisms and lenses, according to the purpose for which it is designed. One of the simplest cases is the refraction of a plane glass, such as the pane of a window.

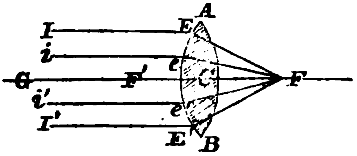
Let IC, fig. 10, be a ray incident on the upper side, AB, of a plane glass, and CE the refracted ray: at its exit at the under side, A′B′, which is parallel to AB, it will be refracted to the same amount as at its entrance, and will pass on in the direction of E*e*, appearing to an observer at *e* to have come along the line I′E, parallel to its real course IC. Hence, in looking at an object through a window it is not seen in its real position; but as all the rays are similarly affected, the object is not distorted, provided the opposite sides of the glass are really parallel.

Fig. 10.



In studying the influence of curved media on light the same rule is to be observed as in reflection by curved mirrors (page 56): a plane, tangent to the curved surface at each point of incidence, is to be drawn or imagined, and the direction of the ray deduced in reference to that plane. On applying this rule to convex and concave lenses, it is found that the former act like concave mirrors, and tend to collect the refracted rays together; whereas a concave lens, like a convex mirror, tends to scatter them. Figure 11 represents parallel rays falling upon a doubly convex lens, the two curved surfaces of which are shown by the vertical section AB. The ray GF, which falls perpendicularly, goes without deviation through the middle or *axis* of the lens. The other rays enter and quit the lens so as to form a smaller angle on one side than on the other, and the acute angle obviously lies on the side towards the axis; every ray is bent towards that axis by both surfaces; and as, from the figure of the lens, the rays most distant from the axis approach the lens at the smallest angle, they also suffer the greatest refraction. The result is, that the rays converge and meet at a point F, termed the *focus* of *parallel rays*, or the *principal focus*. Its distance from C varies both with the curvature of the lens and the refracting power of the glass with which it is made. With glass of the same quality the focal distance depends on the figure of the lens, the greatest convexity giving the shortest focal distance.

Fig. 11.

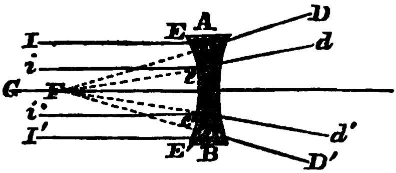


As the lens in figure 11 brings parallel rays into a focus at F, it is obvious that rays diverging from a luminous object placed at F will be rendered parallel by the same lens, the course of the rays being simply reversed. Were a light situated between F and C, its rays would diverge so much that the lens could not render them parallel, and they would continue divergent after refraction. On removing the light to the right of F, the incident rays have such diminished divergence that they converge after refraction, and meet at a certain distance to the left of the lens, which distance diminishes as the light recedes from F; until at length, when the luminous object is so far on the right side of the lens that the incident rays may be considered parallel, they will be bent into a focus at F'.

Convex lenses are subject to the defect called *spherical aberration* equally with concave mirrors (page 56), and from the same cause. The spherical figure of a convex lens causes undue refraction of the rays incident near its margin, so that such rays have a shorter focal distance than those incident near its axis. The defect is more conspicuous in lenses of considerable curvature than in flat ones; and it may be remedied by intercepting the marginal rays with an opaque screen, or by forming such a combination of lenses, as may augment the convergence of the rays near the axis without equally acting on those more distant from it. In the eye this evil is averted by the substance of the lens increasing in density from its margin to the axis.

The action of concave lenses, fig. 12, is the opposite to that of convex lenses. Drawing a tangent to any point of the curve, and constructing the sines of incidence and refraction, as in figure 9, it will be found that parallel rays will be so refracted by both surfaces of a doubly concave lens, that they will diverge as if they had emanated from a common point F before the lens, termed its principal focus, the position of which depends on the refracting power of the substance of the lens, as well as on its curvature. Conversely, the rays D' D, *d*, *d'*, converging towards the principal focus F of a doubly concave lens, will be rendered parallel by such lens: if their original convergence were less rapid, they would diverge after refraction; but if their convergence were to a point between F and C, they would still converge after refraction, and meet somewhere along the axis FG, at a point less remote the greater the original convergence. Rays already di-

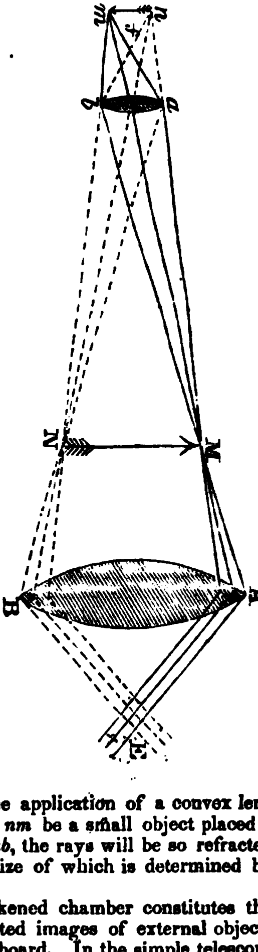
Fig. 12.



vergent will diverge still more after passing through a concave lens. Thus the influence of concave lenses, whether concave on both sides or on one only, is exactly opposed to that of convex lenses. The former tend to diminish or destroy convergence, and to render diverging rays still more divergent; whereas the latter diminish or destroy divergence, and give increased convergence to rays already convergent.

The refracting properties of convex lenses are extensively applied in the construction of *refracting* telescopes and microscopes, the object being, as in *reflecting* telescopes and microscopes, to obtain a distinct small image of a large distant object, or a magnified representation of a near small object. The nature of such combinations is illustrated by the annexed wood-cut, Fig. 13, in which *ab* is a doubly convex lens acting on rays from a distant object represented by the arrow MN. As the incident rays are not parallel, but divergent, the rays from each point of MN will be collected into a focus at a distance behind *ab*, somewhat greater than the focus of parallel rays *f*; and an inverted image *nm* will be produced. The length of the image to that of the object will be directly as their respective distances from the centre of the lens *ab*, exactly as in the reflecting telescope (page 57). If MN is well illuminated, its image will be bright, since each point is formed by the confluence of many rays. The image will be inverted, the rays which emanate from the upper part of the object forming the lower part of the image, and conversely. The direction in which the rays from any point M meet, may be found by drawing a straight line from M through the centre *c* of the lens *ab*; for as the ray MC enters the lens above the axis at the same distance as it quits it below the axis, the second refraction is exactly the reverse of the first, and the ray emerges as though it had passed through a *plane* glass (fig. 10), —moving onwards, not strictly in the same straight *line*, (though for convenience it is usually represented as such,) but in a line parallel to it. Figure 13 likewise exhibits the application of a convex lens in the construction of a microscope. For if *nm* be a small object placed a little beyond the principal focus of the lens *ab*, the rays will be so refracted as to form a large inverted image MN, the size of which is determined by the rule above mentioned.

Fig. 13.

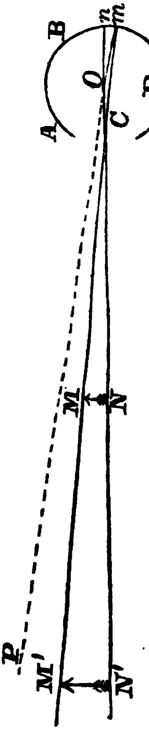


A convex lens fitted into the wall of a darkened chamber constitutes the arrangement of a *camera obscura*, the inverted images of external objects being received on a disk of paper or a white board. In the simple telescope the lens is placed at the extremity of a tube of such length that the image may be formed within the tube, and the observer looks from the other end at the image formed in the air. The eye acts on the same principle. Luminous rays entering the transparent parts of the eye are refracted by the cornea and crystalline lens, and are brought into a focus at the bottom of the eye, an inverted image of external objects being formed upon the retina as on the table of a camera obscura. For distinct vision it is necessary that this image should be formed exactly on the retina. Hence were the eye an ordinary lens, having an invariable focus, our range of vision would be very narrow: an eye fitted for seeing at a distance, would be useless for near objects; and persons who could see near objects, would be blind to remote ones. Two rays emanating from a distant point cannot *both* fall upon so small an object as the eye, unless they are nearly parallel; for if they diverged by even a very small angle, they would before reaching the eye separate by an interval exceeding the diameter of the cornea. On the contrary, rays in rapid divergence may enter the eye, provided the point from which they emanate be close to it; and the nearer the object, the more divergent the rays which enter. When, therefore, we observe a distant landscape, then successively notice nearer and nearer objects, and lastly cast the eyes upon the page of a book only six inches distant, we receive rays coming from a multitude of different objects, each set of rays having its own peculiar divergence, and requiring a separate focus; and yet, so wonderful is the adjusting power of the eye, a single minute suffices for distinctly seeing all the objects so beheld, without the consciousness of an effort.

The adjustment of the eye for different distances appears to depend on a power of increasing or decreasing the distance between the posterior part of the eye and the lens, though the mechanism by which this is accomplished is unknown. Some ascribe it to a change in the figure of the whole eyeball, produced by the muscles which move the eye; but Sir D. Brewster, I think with better reason, considers the position of the lens to be varied by the same contractile tissue which determines the movements of the iris and the size of the pupil. To this adjusting power, however, there is a limit. The distance at which most persons see small objects distinctly is about six inches: at shorter distances the rays are so divergent, that their focal point falls behind the retina, and indistinct vision is the consequence. Persons called *long-sighted* are unable to see near objects distinctly, owing to a weak refracting power of the eye, due to deficient convexity or density in the humours of the eye. This is the infirmity of advancing life, and is remedied by convex glasses, which cause diverging rays to be parallel or slightly convergent. In *short-sighted* persons the refractive power, either from undue convexity or undue density of the cornea and lens, is so powerful, that all rays which do not diverge rapidly are brought to a focus before they reach the retina. Youth is the period most obnoxious to this imperfection, and assistance is derived from a concave glass, which causes parallel rays to diverge, and thereby counteracts the refracting influence of the eye.

Objects are seen erect though their images on the retina are inverted. The direction in which each point of an object is seen, may depend either on the direction of the rays which form it, or on the part of the retina which is impressed. On inspecting the image *nm*, figure 13, it will be seen that any point *n* is formed by a multitude of rays lying within the angle *bna*, each of which has a different direction from the others; and yet when a similar collection of rays is formed on the retina, the observer sees only one point N, situated nearly in the direction of *n*c*N*. Such and similar considerations justify the belief, that the direction in which a luminous point is seen depends not on the direction of the rays as they enter the eye, but on the part of the retina which is impressed. Sir D. Brewster contends that the line of visible direction is always perpendicular to that part on which a ray falls; and that, as the eye-ball is nearly a perfect sphere, these perpendiculars must all pass through the centre of the eye, which he regards as the *centre of visible direction*. To me his arguments do not appear conclusive. Were this opinion true, the point M′ of an arrow M′N′, figure 14, would be seen along the dotted line *m*O*P*, appearing at a spot very remote from its real position. It seems more consistent with observation to take the centre of the crystalline lens, or rather of the collective humours of the eye regarded as one lens, as the centre of visible direction. Through that centre C, fig. 14, all the directions pass from each part of an image, and these cross each other: the lowest part of an image is the highest of the object, and the highest of the image the lowest of the object. It has been supposed that in infancy we actually see erect objects inverted, and only discover that they are not so by the habitual correction derived from experience; but this fallacy has been fully corrected by observation on persons born blind, who first obtained the power of vision when of an age to express what they saw.

Fig. 14.



The apparent size of objects depends on their distance from the eye. Let MC, NC, fig. 14, be rays from the extreme points of the arrow MN, which cross within the eye at C: then the angle MCN is termed the *visual angle*. Mere inspection of the figure shows that the larger that angle is, the greater will be the arc on the retina occupied by the image *mn;* and also the greater that image, the greater will be the angle included by the lines of visible direction. The visual angle in fact varies exactly as the arc of the image; and as that angle may be found with sufficient accuracy by drawing lines from the eye to the extremity of an object, it affords a convenient expression for the length of the image: when the angles are small, the linear magnitudes of two objects are nearly in the same ratio as their visual angles. If a second arrow M'N', twice as long as MN, be placed parallel to MN, and at double its distance from the eye, then, by the properties of similar triangles, their visual angles will be equal, and their apparent magnitude identical. Conversely, if the two arrows be parallel, have the same visual angle or apparent magnitude, and one be twice as distant as the other, the more remote one must be twice as long as the other. The apparent magnitude of the *same* object at different distances may be inferred on the same principles. Thus if MN approach the eye, remaining upright all the time, the visual angle will enlarge, and at half the distance its length will appear double; or if MN recede from the eye, it will be seen under a smaller angle, and appear proportionally smaller, until at double the distance it will seem to be half of its original length. In fact, the apparent length of an object increases in the same ratio as its distance from the eye, or more strictly from the point C within the eye, decreases. A large object seems a mere speck at a great distance; and a minute object is invisible unless brought close to the eye. To bring an object near the eye is to magnify it. A tower which appears 100 feet high to a person 4 miles distant, will seem 200 feet high at 2 miles, and 400 at 1 mile; and the type of a book which at 12 inches appears a line in length, will appear two lines at 6 inches. In these cases it is the *linear* magnitude which varies inversely as the distance: the superficial extent, or area, will vary inversely as the square of the distance.

The foregoing considerations account for many optical phenomena. Short-sighted persons see minute objects better than those who have a long sight, because, from the greater refractive power of their eyes (page 62), they can bring the object closer to the eye than those who are long-sighted, and therefore see it under a greater angle. But byaid of a convex lens a long-sighted person may attain the same end. Let him place the object in the focus of a convex lens, and the eye at a distance behind convenient for receiving all the rays which pass through it: the diverging rays, rendered parallel by the lens, are readily formed by the eye into an image on the retina, and the object is seen under the same angle as though the eye had occupied the position of the lens. This arrangement is shown by figure 13, where MN is the object, AB the lens, and E the eye of the observer. If the focal distance of the lens be 1 inch, we gain the same advantage as though the eye itself were placed at one inch; and taking 6 inches as the shortest distance of distinct vision with the unaided eye, the apparent length of the arrow will be increased in the ratio of 1 to 6. With a lens of half an inch focus, the increase will be as $\frac{1}{2}$ to 6, or 1 to 12; and if the focus is $\frac{1}{10}$th of an inch, the increase will be as $\frac{1}{10}$ to 6, or 1 to 60. Convex lenses are hence familiarly known by the name of *magnifying glasses.*

Convex lenses are similarly employed in the construction of compound microscopes and telescopes. In figure 13, let *nm* represent a small object formed by the lens *ab* into an enlarged image MN: that image may be viewed by the eye at the distance of 6 inches; but by interposing a second lens AB of 1 inch focal distance, the effect is the same as though the eye were at 1 inch, and thus the image is further increased in the ratio of 1 to 6. The lens AB is called the *eye-glass*, and *ab* the *object-glass*. Again, in a telescope, a large distant object is represented as a minute image, and so far its magnifying power depends on the eye being able to inspect a small image at 6 inches instead of the large object at a great distance. For instance, a tower 400 feet high, formed into an image 1 foot long, is thereby shortened 400 times; but as that image can be seen distinctly at the distance of $\frac{1}{2}$ a foot instead of the object at 400 feet, the elongation due to this cause alone is as 1 to 800. The apparent height of the tower is thus diminished 400 times by one cause, and increased 800 times by another; so that the compound effect is, that it is doubled. But by employing a second lens with a very short focus, the image may be still further magnified to a great extent.

Double Refraction.—If on a piece of paper with a black line on its surface we place a rhombohedron of Iceland-spar, and then look at the line through the crystal, it will be found that in a certain position the line appears single as when seen through water or glass; but in other positions of the crystal two lines are visible parallel to each other, and separated by a distinct interval. The light in passing through the crystal is divided into two portions, one of which obeys the laws of refraction already explained (page 58); whereas the other portion proceeds in a wholly different direction, and hence gives the appearance of two objects instead of one. The former is termed the *ordinary*, the latter the *extraordinary* ray. This phenomenon is known by the name of *double refraction*, and has been witnessed in many crystallized substances, as in minerals and artificial salts.

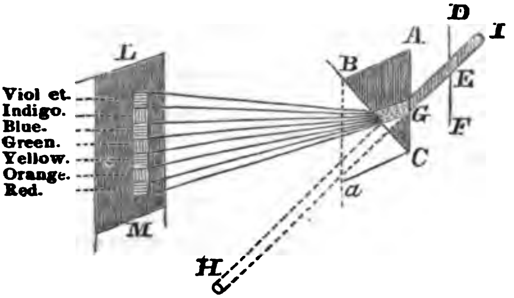
Light, transmitted through Iceland-spar or other doubly refracting substances, is found to have suffered a remarkable change. In this state it is distinguished from common light by the circumstance, that when it falls upon a plate of glass at an angle of 56° 11′, it is almost completely reflected in one position of the glass, and is hardly reflected at all in another: if reflected when the plane of reflection is vertical, no reflection ensues when the reflecting plane is horizontal, the incident angle being maintained at 56° 11′. This curious property, so different from common light, has been theoretically ascribed to a kind of *polarity* of such sort, that each side of a ray of light is thought to have a character different from the two adjacent sides at right angles to it; and hence the origin of the term *polarized light*, by which this property is distinguished. Light is polarized by reflection from many substances, such as glass, water, air, ebony, mother-of-pearl, and many crystallized substances, provided the light is incident at a certain angle peculiar to each surface, and which is called the *polarizing angle*. Thus, the polarizing angle for glass is 56° 11′, and for water 53° 14′; that is, common light reflected by glass and water at the angles stated will be polarized.

The phenomena of double refraction and polarized light constitute a department of optics of great and increasing interest; but it is too remote from the pursuits of a chemical student to be treated of at length in this work. Those interested in such studies will find an excellent guide in Sir D. Brewster's Treatise on Optics in the Cabinet Cyclopedia.

DECOMPOSITION OF LIGHT.

The analysis of light may be effected either by refraction or absorption Newton, who discovered the compound nature of solar light, effected its decomposition by refraction, employing a solid piece of glass bounded by three plane surfaces, well known under the name of the *prism*. His mode of operating consisted in admitting a ray of light IG, fig. 15, into a dark chamber through a window-shutter DEF, and interposing the prism ACB, so that the ray should pass obliquely through two surfaces, and be refracted by both. On receiving the refracted ray upon a piece of white paper LM, there appeared, instead of a spot of white light, an oblong coloured surface composed of seven different tints, called the *prismatic* or *solar spectrum*. On subjecting each of these colours to refraction, no further separation was accomplished; but on causing the rays separated by one prism to pass through a second of the same power and in an inverted position CBa, the seven colours disappeared, and a spot of white light appeared at H, in the very position which it would have occupied had both prisms been absent. From such and similar experiments Newton inferred that white light is a mixture of seven *colorific* rays,—red, orange, yellow, green, blue, indigo, and violet; and that the separation of these primary or simple rays depended on an original difference of refrangibility, violet being the most refrangible and red the least so.

Fig. 15.



Though a prism is the most convenient instrument for decomposing light, the separation of the coloured rays is more or less effected by refracting media in general. Lenses, accordingly, disperse the colorific rays at the same time that they refract them; and this effect constitutes one of the greatest difficulties in the construction of telescopes, in so much as the separation or *dispersion*, as it is termed, of these rays diminishes the distinctness of the image. The combinations by which the defect is remedied are called *achromatic*.

Newton's analysis of light led him to explain the origin of the colours of natural objects. Of opaque bodies, those are black which absorb all the light that falls upon them, and those white which reflect it unchanged; the various combinations of tints are the consequence of certain rays being absorbed, while those alone whose intermixture produces the observed colour are reflected. The same applies to transparent media, which are colourless like pure water when the light passes through unchanged, but are coloured when some rays are transmitted and others absorbed. This absorption of certain rays by coloured media, such as glass of different tints, affords another mode of decomposing light; and Sir D. Brewster has ingeniously applied it to analyze the seven colours which compose the prismatic spectrum. He has proved by such experiments, what has been maintained before, that the seven colours of the spectrum are occasioned not by seven but by three simple or primary rays; namely, the red yellow, and blue. These rays are concentrated in those parts of the spectrum where each primary colour respectively appears; but each spreads more or less over the whole spectrum, the mixture of red and yellow giving orange, of yellow and blue, green, and red with blue and a little yellow causing the violet.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power: the orange illuminates in a higher degree than the red, the yellow than the orange. The maximum of illumination lies in the brightest yellow or palest green. The green itself is almost equally bright with the yellow; but beyond the full deep green the illuminating power sensibly decreases. The blue is nearly equal to the red, the indigo is inferior to the blue, and the violet is the lowest on the scale. (Phil. Trans. 1800.)

Solar light, both direct and diffused, possesses the property of exciting heat as well as light. This effect takes place only when the ray is absorbed, the temperature of transparent substances through which it passes, or of opaque ones that reflect it, remaining unchanged. Hence the burning-glass and concave reflector are themselves nearly or quite cool, though at the same time intense heat is developed at the focus. The intense coldness of the higher strata of the air arises from the same cause: the sun's rays pass on unabsorbed through the atmosphere; and its lower strata would also be very cold, did they not receive heat by contact from the earth.

The absorption of light is much influenced by the nature of the surface on which it falls; and it is remarkable that those substances which absorb radiant heat most powerfully, are also the best absorbers of light. Difference of colour has still greater influence over the absorption of light than of simple heat. That dark-coloured substances acquire in sunshine a higher temperature than light ones, may be inferred from the general preference given to the latter as articles of dress during the summer; and this practice, founded on the experience of mankind, has been justified by direct experiment. Dr. Hooke, and subsequently Dr. Franklin, proved the fact by placing pieces of cloth of the same texture and size, but of different colours, upon snow, and allowing the sun's rays to fall upon them. The dark-coloured specimens always absorbed more heat than the light ones, the snow beneath the former having melted to a greater extent than under the others; and it was remarked that the effect was nearly in the ratio of the depth of shade. Sir H. Davy also examined the subject, and arrived at the same conclusions.

Calorific Rays of the Spectrum.—The rays of the prismatic spectrum differ from each other in their heating power as well as in colour, a fact first observed by Sir W. Herschel, whose attention was attracted to it by the circumstance, that, in viewing the sun with large telescopes through differently coloured glasses, he sometimes felt a strong sensation of heat with little light, and at other times he had a strong light with little heat. This observation led to his celebrated researches on the heating power of the prismatic colours. (Phil. Trans. 1800.) The experiments were made by transmitting a solar beam through a prism, receiving the spectrum on a table, and placing the bulb of a very delicate thermometer successively in the different parts of it. While engaged in this inquiry, he observed not only that the red was the hottest ray, but that there was a point a little beyond the red, altogether out of the spectrum, where the thermometer stood higher than in the red itself. By repeating and varying the experiment, he found that the most intense heating power was always beyond the red ray, where there was no light at all; and that the heat progressively diminished in passing from the red to the violet, where it was least. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but not light; and that these rays, from being less refrangible than the luminous ones, deviate in a smaller degree from their original direction in passing through the prism.

All succeeding experimenters confirm the statement of Sir W. Herschel, that the prismatic colours differ in heating power; but they do not agree as to the spot where the heat is greatest. Sir H. Englefield, Davy, and others affirmed with Herschel that it is beyond the red ray; while others, and in particular Leslie, contended that it is in the red itself. The observations of the late Dr. Seebeck (Edin. Jour. of Science, i. 358), have explained those contradictory statements, by showing that the point of greatest heat varies with the kind of prism which is employed for forming the spectrum. When he used a prism of fine flint-glass, the greatest heat was uniformly beyond the red; with a prism of crown-glass, the red itself was the hottest part; and with a prism externally of glass, but containing water within, the maximum heat was neither in the red itself, nor beyond it, but in the yellow. These experiments have been confirmed by Melloni, who has succeeded with a prism of rock-salt in separating the spot of maximum heat from the coloured part of the spectrum by a much greater interval than had been done previously: his curious and surprising results appear to me to dissipate all remaining doubt as to the existence in solar light of calorific rays distinct from those rays which produce colour. He also traces the cause of the varying position of the maximum heat to the unequal absorptive power of different transparent media. Rock-salt is freely transmissible to the least refrangible calorific rays in solar light, but absorbs a greater proportion of those which are more refrangible; whereas the latter pass more easily through flint-glass, yet more readily through crown-glass, and with still greater freedom through water. Hence in successively employing a prism of these four substances in the order stated, the spot of greatest heat is found to be far beyond the red, then approaches the red, next in the red itself, and lastly is in the yellow part of the spectrum.—The preceding facts go far to prove that most, if not all, of the heating power ascribed to light is due, not to the absorption of luminous rays, but to that of the heat by which they are accompanied.

Chemical Rays.—It has long been known that solar light is capable of producing powerful chemical changes. One of the most striking instances of it, is its power of darkening the white chloride of silver, an effect which takes place slowly in the diffused light of day, but in the course of two or three minutes by exposure to sunshine. This effect was once attributed to the influence of the luminous rays; but it appears from the observations of Ritter and Wollaston, that it is owing to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical* rays. It is found that the greatest chemical action is exerted just beyond or at the verge of the violet part of the prismatic spectrum; that the spot next in energy is the violet itself; and that the property gradually diminishes in advancing to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous ones, in consequence of which they are dispersed in part over the blue, indigo, and violet, but in the greatest quantity at the extreme border of the latter.

Magnetizing Rays.—The more refrangible rays of light have been thought to possess the property of rendering steel and iron magnetic. The existence of this property was first asserted by Dr. Morichini of Rome. Other observers subsequently failed in obtaining the same results; but in the year 1826 the fact appeared to be decisively established by the learned and accomplished Mrs. Somerville, in an essay published in the Transactions of the Royal Society. Since that period the subject has been re-examined by MM. Riess and Moser. They object to Mrs. Somerville's results, that her method of ascertaining the magnetic state of the needles used in the experiments was not sufficiently precise: they found that the duration of the oscillations of needles is exactly the same whether they are made to oscillate in the shade or under exposure to the concentrated violet ray of the spectrum, a result which could not occur had even a feeble degree of magnetism been excited; and they accordingly deny the supposed magnetizing power of light. (Edin. Journ. of Science, ii. 225.)

TERRESTRIAL LIGHT.

Under this head are included all kinds of artificial light. The common method of obtaining such light is by the combustion of inflammable matter, which gives out so much heat that the burning substance is rendered luminous in the act of being burned. All bodies begin to emit light when heat is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called *incandescence*. The temperature at which solids in general begin to shine in the dark is between 600° and 700° F; but they do not appear luminous in broad daylight till they are heated to about 1000°. The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. If the temperature still increase, the character of the glow changes, and by degrees it becomes white, shining with increasing brilliancy as the heat augments. Liquids and gases likewise become incandescent when strongly heated; but a very high temperature is required to render a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles, and gas light, are instances of incandescent gaseous matter.

Artificial lights differ in colour, and accordingly exhibit different appearances when transmitted through a prism. The white light of incandescent charcoal, which is the principal source of the light from candles, oils, and the illuminating gases, contains the three primary colorific rays, the red, yellow, and green. The dazzling light emitted by lime intensely heated, first proposed by Lieut. Drummond for the trigonometrical survey (Phil. Trans. 1830), and of late so successfully applied by Messrs. Cooper and Carey for their gas microscope, gives the prismatic colours almost as bright as in the solar spectrum. The light emitted by iron feebly incandescent consists principally of the blue and red rays, as does the red light obtained by means of strontia and lithia; that from ignited boracic acid is such a mixture of the blue and yellow rays as constitutes green; and incandescent soda emits a yellow light, almost wholly free from the rays which cause the red and blue colours.

Artificial light differs from solar light in containing heat in two states. It contains simple radiant heat like that radiated from a body not luminous, and which may be separated by transmission through a plate of moderately thick glass; but the light so purified still heats any body which absorbs it, and is thus believed to possess calorific rays associated with its luminous rays like those in solar light, and like them to be susceptible of refraction by transparent media. Thus, Mr. Daniell found that the rays from incandescent lime were concentrated by convex lenses, and set fire to phosphorus placed in the focus. (Phil. Mag. N. S. ii. 59.) The heat excited under such circumstances may of course be ascribed to the absorption of luminous rays; but the experiments of Herschel with solar light suggest the idea that calorific rays capable of transmission through glass may also exist in artificial light, and this opinion has been verified by the late researches of Melloni. Nothing could show the fact in a more distinct point of view than the discovery, by this ingenious experimenter, that transparent media are *unequally* permeable by colorific and calorific rays: substances almost opaque in regard to light, were found to give free passage to calorific rays; while others of the most perfect transparency are little permeable to heat. Melloni has consequently introduced a distinct name, *diathermanous* (from διὰ and θερμαίνω) to denote free permeability to heat, just as diaphanous is formed from διὰ and φαίνω. Rock-salt is remarkably diathermanous or *transcalent*, greatly more so than glass of far greater transparency. Chloride of sulphur of a reddish-brown tint is more diathermanous than nut and olive oil of a light yellow colour, and these than the purest ether, alcohol, and water, the transparency of these substances being in the opposite order. A great many facts of a like kind are enumerated in Melloni's essay, which is highly deserving of attention. The source of heat was an argand oil-lamp, and the temperature measured by the thermo-multiplier (page 11). (An. de Ch. et de Ph. liii. 5.)

The chemical agency of artificial light is analogous to that from the sun. In general the former is too feeble for producing any visible effect; but light of considerable intensity, such as that from ignited lime, darkens chloride of silver, and seems capable of exerting the same chemical agencies as solar light, though in a degree proportionate to its inferior brilliancy. (An. of Phil. xxvii. 451.)

Light is emitted by some substances either at common temperatures or at a degree of heat disproportioned to the effect, giving rise to an appearance which is called *phosphorescence*. This is exemplified by a composition termed *Canton's phosphorus*, made by mixing three parts of calcined oyster-shells with one of the flowers of sulphur, and exposing the mixture for an hour to a strong heat in a covered crucible. The same property is possessed by chloride of calcium (Homberg's phosphorus), anhydrous nitrate of lime (Baldwin's phosphorus), some carbonates and sulphates of baryta, strontia, and lime, the diamond, some varieties of fluor-spar called *chlorophane*, apatite, boracic acid, borax, sulphate of potassa, sea-salt, and by many other substances. Scarcely any of these phosphori act unless they have been previously exposed to light: for some, diffused day-light or even lamp-light will suffice; while others require the direct solar light, or the light of an electric discharge. Exposure for a few seconds to sunshine enables Canton's phosphorus to emit light visible in a dark room for several hours afterwards. Warmth increases the intensity of light, or will renew it after it has ceased;—but it diminishes the duration. When the phosphorescence has ceased it may be restored, and in general for any number of times, by renewed exposure to sunshine; and the same effect may be produced by passing electric discharges through the phosphorus. Some phosphori, as apatite and chlorophane, do not shine until they are gently heated; and yet if exposed to a red heat, they lose the property so entirely that exposure to solar light does not restore it. Mr. Pearsall has remarked that in these minerals the phosphorescence, destroyed by heat, is restored by electric discharges; that specimens of fluor-spar, not naturally phosphorescent, may be rendered so by electricity; and that this agent exalts the energy of natural phosphori in a very remarkable degree. (R. Inst. Journal, N. S. i.)—The theory of these phenomena, like that of light itself, is very obscure. They have been attributed to direct absorption of light, and its subsequent evolution; but the fact, that the colour of the light emitted is more dependent on the nature of the phosphorescent body than on the colour of the light to which it was exposed, seems inconsistent with this explanation. Chemical action is not connected with the phenomena; for the phosphori shine *in vacuo*, and in gases which do not act on them, and some even under water.

Another kind of phosphorescence is observable in some bodies when strongly heated. A piece of lime, for example, heated to a degree which would only make other bodies red, emits a brilliant white light of such intensity that the eye cannot support its impression.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has set in. Sea-water is capable of dissolving the luminous matter; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phosphorescent.

Light is sometimes evolved during the process of crystallization. This is exemplified by a tepid solution of sulphate of potassa in the act of crystallizing; and it has been likewise witnessed under similar circumstances in a solution of fluoride of sodium and nitrate of strontia. Another instance of the kind is afforded by the sublimation of benzoic acid. Allied to this phenomenon is the phosphorescence which attends the sudden contraction of porous substances. Thus, on decomposing by heat the hydrates of zirconia, peroxide of iron, and green oxide of chromium, the dissipation of the water is followed by a sudden increase of density suited to the changed state of the oxide, and a vivid glow appears at the same instant. The essential conditions are, that a substance should be naturally denser after decomposition than it was previously, and that the transition from one mechanical state to the other should be abrupt.

It is sometimes of importance to measure the comparative intensities of light, and the instrument by which this is done is called a *Photometer*. The only photometer which is employed for estimating the relative strength of the sun's light is that of Leslie. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the light that falls upon it, and, therefore, its temperature is not affected; they are all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, cause the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the heat produced by the absorption of light. Leslie conceives that light when absorbed is converted into heat; but according to the experiments already referred to, the effect must be attributed, not so much to the light itself, as to the absorption of the calorific rays by which it is accompanied.

Sir J. Leslie recommended his photometer also for determining the relative intensities of artificial light, such as that emitted by candles, oil, or gas. This application of it differs from the foregoing, because light proceeding from terrestrial sources contains heat under two forms. One portion is analogous to that emitted by a hot body which is not luminous; the other is similar to that which accompanies solar light. It is presumed that the first form of heat will not prove a source of error; that these rays are wholly intercepted by the outer case of glass; or that, should a few penetrate into the interior, they will be absorbed equally by both balls, and will therefore heat them to the same extent. It is probable that this reasoning is not wide of the truth; and, consequently, the photometer will give correct indications so far as regards the new element—non-luminous heat. But it is not applicable to lights which differ in colour, because the relation between the heating and illuminating power of such lights is exceedingly variable. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and, consequently, they may and do produce a greater effect on the photometer than some lights whose illuminating powers are far stronger.

The second kind of photometer is on a totally different principle. It determines the comparative strength of lights by a comparison of their shadows. This instrument was invented by Count Rumford, and is described by him in his Essays. It is susceptible of great accuracy when employed with the requisite care;* but, like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best mode of obtaining an approximative result, is by observing the distance from each light at which any given object, as a printed page, ceases to be distinctly visible.] The illuminating power of the lights so compared is as the squares of their distances.

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* See an Essay on the construction of Coal Gas Burners, &c. in the Edinburgh Philosophical Journal for 1825.

SECTION III.

ELECTRICITY.

Elementary Facts.—When certain substances, such as amber, glass, sealing-wax and sulphur, are rubbed with dry silk or cloth, they are found to have acquired a property, not observable in their ordinary state, of causing contiguous light bodies to move towards them; or if the substances so rubbed be light and freely suspended, they will move towards contiguous bodies. After a while this curious phenomenon ceases; but it may be renewed an indefinite number of times by friction. The principle thus called into action is known by the name of *electricity*, from the Greek word ηλεκτρον, amber, because the electric property was first noticed in it. The same term is applied to the science which treats of the phenomena of electricity.

When a substance by friction or any other means acquires the property just stated, it is said to be *electrified*, or to be *electrically excited;* and its motion towards other bodies, or of other bodies towards it, is ascribed to a force called *electric attraction*. But its influence, on examination, will be found to be not merely attractive; on the contrary, light substances, after touching the electrified body, will be disposed to *recede* from it just as actively as they approached it before contact. This is termed *electric repulsion*. By aid of the electrical machine these phenomena of electric attraction and repulsion may be displayed by a great variety of amusing and instructive experiments, showing how readily an invisible power is called into operation, and how wonderfully inert matter is subject to its control. But the student may witness these effects quite satisfactorily by very simple apparatus. Let him suspend a thread of white sewing silk from the back of a chair so that one end may hang freely, taking the precaution to moisten that end slightly by holding it between the fingers, while the rest of the thread is carefully dried by the fire; and let him then place near the free end a piece of sealing-wax previously rubbed on the sleeve of his coat. The silk will move towards it; but after touching the excited wax two or three times, it will recede from it.

When an electrified body touches another which is not electrified, the electric property is imparted by the former to the latter. Thus, on touching the free end of the suspended silk thread with the excited wax, the silk will itself be excited, as shown by its moving towards a book, a knife, or other unexcited object placed near it. But though electricity is always imparted by an excited to an unexcited body by contact, the latter does not always exhibit electric excitement. If, for example, the suspended silk be wetted along its whole length, it will be strongly attracted by the excited wax, but after contact it will not evince the least sign of being itself electrified. Nevertheless, electricity is commmunicated to the silk in both cases, only it is retained by silk when dry, and is lost as soon as received by wet silk. Such observations led to the discovery that electricity passes with great case over the surface of some substances, and with difficulty over that of others, and hence to the division of bodies into *conductors* and *non-conductors* of electricity. If electricity be imparted to one end of a conductor, such as a copper wire, the other extremity of which touches the ground, or is held by a person standing on the ground, the electricity will pass along its whole length and escape in an instant, though the wire were several miles long; whereas excited glass and resin, which are non-conductors, may be freely handled without losing any electricity except at the parts actually touched. To this class of conductors belong the metals, charcoal, plumbago, water, and aqueous solutions, and substances generally which are moist or contain water in its liquid state, such as animals and plants, and the surface of the earth. These, however, differ in their conducting power: of the metals, Mr. Harris found silver and copper to be the best conductors, and after these follow gold, zinc, platinum, iron, tin, lead, antimony, and bismuth. (Phil. Trans. 1827, Part i. 21.) Mr. Forbes has lately called attention to the fact that the foregoing order is very nearly the same as that expressive of their conducting power for heat. Aqueous solutions of acids and salts conduct much better than pure water. To the list of non-conductors belong glass, resins, sulphur, diamond, dried wood, precious stones, earth and most rocks when quite dry, silk, hair, and wool. Air and gases in general are non-conductors if dry, but act as conductors when saturated with moisture.

This knowledge is of continual application in electrical experiments. When it is wished to collect electricity on a metallic surface, the metal must be *insulated*, that is, cut off from contact with the earth, and with conductors touching the ground, by means of some non-conductor; an object commonly effected either by supporting it on a handle of glass, or by placing it on a stool made with glass feet. Another mode of insulating is to suspend a substance by silk threads. But such insulators must be dry; since they begin to conduct as soon as they grow damp, and conduct well, as in the experiment above described, when wet. Again, electrical experiments are very apt to fail in damp weather, because the moisture both carries off electricity directly, and by being deposited on the glass supports, destroys the insulation.

To diminish this inconvenience it is usual to keep the insulators warm, and to coat them with a varnish made by dissolving the resin called shell-lac in alcohol, this resinous matter being much less prone to attract moisture from the air than glass. The same principles account for an error once prevalent that a metal cannot be excited by friction: if held in the hand, indeed, it exhibits no sign of excitement when rubbed, because the electricity is carried off as soon as excited; but if, while carefully insulated, it is rubbed with a dry cat's fur, excitement readily ensues.

On comparing the electric properties manifested by glass and sealing-wax when both are rubbed by a woollen or silk cloth, they will be found essentially different; and hence it is inferred that there are two kinds or states of electricity, one termed *vitreous*, because developed on glass, and the other *resinous* electricity, from being first noticed on resinous substances. These two kinds of electricity, one or other of which is possessed by every electrified substance, are also termed *positive* and *negative*, the terms *vitreous* and *positive* being used synonymously, as are *resinous* and *negative*. The mode of distinguishing between positive and negative electricity is founded on the circumstance, that if two electrified substances are both positive or both negative, they are invariably disposed to recede from each other, that is, to exhibit electric repulsion; but if one be positive, and the other negative, their mutual action is as constantly attractive. The end of a silk thread, after contact with an electrified stick of sealing-wax, is repelled by the wax, because both are in the same electric state; but if a dry warm wine-glass be rubbed with cloth or silk, and then presented to the thread, attraction will ensue. A silk thread, in a *known* electric state, thus indicates the kind of electricity possessed by other substances: a convenient mode of doing this, is to draw a thread of white silk rapidly through a fold of coarse brown paper previously warmed, by which means its whole length will be rendered positive.

When two substances are rubbed together so as to electrify one of them, the other, if in a state to retain electricity, will be excited also, one being always negative and the other positive. It is easy to be satisfied of this by very simple experiments. Rub a stick of sealing-wax on warm coarse brown paper, and the paper will be found to repel a positively excited thread of silk, while the wax will attract it; if a warm wine-glass be rubbed on the brown paper, the glass will be positive, as shown by its repelling the positive thread, while the same thread will be attracted by the negative paper; friction of sealing-wax on a silk riband renders the wax negative and the riband positive, but with glass the riband is negative. If two silk ribands, one white and the other black, be made quite warm, placed in contact, and then drawn quickly through the closed fingers, they will be found on separation to be highly attractive to each other, the white being positive and the black negative. The back of a cat is positive to all substances with which it has been tried, and smooth glass is positive to all except the back of a cat. Sealing-wax is negative to all the substances just enumerated, but becomes positive by friction with most of the metals. The reader will perceive from these facts that the same substance may acquire both kinds of electricity, becoming positive by friction with one body, and negative with another.

THEORIES OF ELECTRICITY.

The nature of electricity, like that of heat and light, is at present involved in obscurity. All these principles, if really material, are so light, subtile, and diffusive, that it has hitherto been found impossible to recognize in them the ordinary characteristics of matter; and, therefore, electric phenomena might be referred, not to the agency of a specific substance, but to some property or state of common matter, just as sound is produced by a vibrating medium. But the effects of electricity are so similar to those of a mechanical agent; it appears so distinctly to emanate from substances which contain it in excess, and rends asunder all obstacles in its course so exactly like a body in rapid motion, that the impression of its existence as a distinct material substance *sui generis* forces itself irresistibly on the mind. All nations, accordingly, have spontaneously concurred in regarding electricity as a *material* principle; and scientific men give a preference to the same view, because it offers an easy explanation of phenomena, and suggests a natural language easily intelligible to all.

Theory of Two Electric Fluids.—This theory, the fundamental facts of which were supplied partly by Dufay, and partly by Symmer, is founded on the assumed existence of two electric fluids, which Dufay distinguished by the terms *vitreous* and *resinous* electricity. In order to account for electric phenomena by this supposition, the two fluids are assumed to possess the following properties:—They are both equally subtile and elastic, universally diffused, and, therefore, present in all bodies, possessed of the most perfect fluidity, each highly repulsive to its own particles, and as highly attractive to those of the opposite kind; these attractive and repulsive forces being exactly equal at the same distance, and both varying inversely as the square of the distance varies. Electric quiescence is ascribed to these fluids being combined and neutralized with each other; and electric excitation is the consequence of either fluid being in excess. Their combination is destroyed by several causes, of which friction is one. The application of these principles is as follows. Two unexcited contiguous bodies, A and B, are electrically indifferent to each other; for, though each electricity in A repels the electricity of the same name in B, attraction to precisely the same extent is exerted between the opposite electricities, and no change results. If A and B are rubbed together, a portion of the combined electricities in both is decomposed, and the separated resinous fluid is transferred to one of them, suppose to A, and the vitreous to B, each being electrified to the same degree, though oppositely. The free particles of resinous electricity in A tend by their repulsion to recede from each other, and would quit A altogether, unless their passage were impeded by a non-conductor: the atmosphere, if dry, cuts off the retreat, and by its pressure confines the resinous fluid to the surface of A. The same happens to the vitreous fluid on the surface of B. But the opposite electricities fixed on A and B exert a strong mutual attraction, and may succeed either in forcing their way across the intervening stratum of air, or of actually drawing A and B into contact. In either case the free electricities reunite, and the electric equilibrium is restored. On the contrary, if A and a are similarly electrified, that is, possess the same kind of free electricity, the effort of the electric fluid to escape in opposite directions causes the substances themselves to fly asunder, if the repulsive force exceed their weight, and thus produces electric repulsion.

This theory, as commonly stated, takes little or no cognizance of any attraction between the electric fluids and other material substances. But it would be against all analogy to suppose no such influence to exist; and indeed the supposition of an attractive force acting at insensible distances seems necessary to account for the impediment caused by non-conductors to the free movement of the electric fluids.

Theory of a Single Fluid.—The celebrated American philosopher, Franklin, proposed a different theory, founded on the supposition of a single electric fluid, the particles of which are conceived to repel each other with a force diminishing as the squares of the distance, and to be attracted by matter in general according to the same law. Material substance in its unelectric state is regarded as a compound of electricity and matter, saturated and neutralized with each other. It is also an assumption, shown to be necessary by Æpinus and Cavendish, that ponderable bodies repel each other with the same force and according to the same law as the particles of electricity. From the nature of these postulates it will be easy to anticipate their application. Unelectric bodies are such as have their natural quantity of electricity, which precisely suffices to saturate and neutralize the matter of which they consist. They are then electrically indifferent; because the repulsion exerted between the electricity and matter of contiguous bodies is exactly counteracted by the attraction of the electric fluid in each for the matter of the other. Electrical excitement is occasioned either by increase or diminution of the natural quantity of electricity. On rubbing a tube of glass with a woollen cloth, the electric condition of both is disturbed: the glass acquires more electricity than it naturally possesses, or is overcharged with electric fluid; and the cloth, losing what the glass gained, contains less than its natural supply, or is under-charged. These opposite states are denoted by the algebraic terms *positive* and *negative*, the former corresponding to the vitreous, the latter to the resinous electricity of Dufay. Bodies, positively excited, repel each other by means of the repulsion among the particles of the electricity with which they are surcharged; and the equal tendency of negatively excited bodies to separate is ascribed to the mutual repulsion among the particles of matter. The electric equilibrium in excited substances is restored by the electricity escaping from those where it is in excess, and passing to those which are under-charged.

To the theory of Franklin it is objected that it involves an assumption at variance with the laws of gravitation, namely, that of matter being repulsive to itself; but in fact this assumption, if admitted, would not satisfactorily explain the unequal distribution of the electric energy over the surface of the electrified bodies, as well negative as positive, dependent on their form. To account for this phenomenon the theory requires a repulsive fluid superadded to matter, and freely moveable among its particles, a sort of resident electric fluid, capable of performing all the functions ascribed to resinous electricity. With such addition, however, the theory of Franklin would virtually cease to be that of a single electric fluid, and would still, I suspect, be less generally applicable than the theory of two fluids. I feel it necessary, accordingly, to adopt the latter, substituting, however, agreeably to present usage, the terms *positive* and *negative* for *vitreous* and *resinous* electricity.*

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* The chief objection which has been urged against the Franklinian theory of one electric fluid is, that it fails to explain the repulsion of two negatively electrified bodies. It is alleged that the condition of two bodies, the essence of which consists in the absence of a subtle principle called electricity, cannot cause them to repel each other; for this would be attributing to a negation the possession of a positive property, which is absurd. It was

CAUSES OF ELECTRIC EXCITEMENT.

Friction.—This cause of electric excitement having been already mentioned, it here only remains to state the usual modes of developing electricity by friction. A supply of negative electricity is easily obtained by rubbing a stick of sealing-wax, or a glass tube covered with sealing-wax, with silk or woollen cloth; and positive electricity is freely developed when a dry glass tube is rubbed with silk, brown paper, or flannel, the surface of which is covered with a little amalgam. But for obtaining an abundant supply of electricity it is necessary to employ an electrical machine, which is a mechanical contrivance for exposing a large surface of glass to continuous friction. As now constructed, it is formed either with a cylinder or plate of glass which is made to revolve upon an axis, and pressed during rotation by cushions or rubbers made of leather stuffed with flannel, and covered usually with silk. On the rubber is spread an amalgam of tin and zinc, rendered adhesive by admixture with a small quantity of lard or tallow. To prepare the amalgam, melt in a Hessian crucible one ounce of tin and three of zinc, then add two ounces of mercury heated to near its boiling point, stir briskly with a stick for a few minutes, and pour the mixture on a clean dry stone: when cold pulverize and sift, and preserve the fine powder in a well-corked dry phial. Another essential part of the machine is the *prime conductor*, which is an insulated conductor, commonly made of brass, placed in such immediate proximity to the revolving glass, that the electric state of the one is instantly imparted to the other.

The electricity developed by the electrical machine is due partly to friction, which disunites the combined electric fluids of the glass and rubber, but principally to the oxidation of the amalgam. The positive fluid is transferred to the glass, from it to the contiguous prime conductor, and thence to any system of conductors connected with the prime conductor; and similarly the negative fluid collects upon the rubber, whence it is distributed to one or more conductors with which the rubber may be in connexion. Thus all insulated conductors in contact with the prime conductor are positive, and those attached to the rubber are negative. When once the glass and rubber are excited, it is necessary that the electric equilibrium of both should be restored before a second development can occur; and accordingly it is found that very little electricity is obtained when the prime conductor and rubber's conductor are both insulated. On taking positive electricity from the prime conductor, the rubber should communicate with the ground, that its negative electricity might escape; and when negative electricity is taken from the rubber's conductor, the prime conductor is connected with the ground. The same object may be accomplished by connecting the prime conductor with the rubber's conductor, though in experiments it is commonly inconvenient to employ this arrangement.

Change of Temperature.—The operation of this cause of electric excitement was first noticed in certain minerals, such as tourmalin and boracite, not possessed of that symmetric arrangement of parts commonly observed in crystals, and which are electrified by the application of heat. But a far more general principle was detected by the late Dr. Seebeck, who found that the electric equilibrium is disturbed in certain metallic rods or wires when one extremity has a different temperature from that of the other, whether

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this apparent difficulty which induced Æpinus and Cavendish to assert that the theory of Franklin required the assumption that matter was repulsive to itself. Loaded with this postulate, the theory may, indeed, be untenable; but the question arises, whether, in point of fact, the postulate mentioned is necessary to the Franklinian theory. We think it is not; but are inclined, with Dr. Hare, to refer the apparent repulsion of negatively electrified bodies to an attraction between such bodies and the contiguous air, electrified positively by induction.—*Ed.*

the difference be effected by the application of heat or cold. This observation has been since shown by Professor Cumming to be true of all metals. (An. of Phil. N. S. v. 427.) See also the recent experiments by Mr. Prideaux. (Phil. Mag. iii.) The experiment is usually made by heating or cooling the point of junction of two metallic wires, which are soldered together; but M. Becquerel has proved that the contact of different metals is not essential. (An. de Ch. et de Ph. xli. 353.)

Chemical Action.—Another, and very fertile source of electricity, is chemical action. This was strongly denied by the late Sir H. Davy in his Bakerian lecture for 1826; but the experiments of Becquerel, De la Rive, and Pouillet, afford decisive proof that chemical union and decomposition are both attended with electrical excitement. (An. de Ch. et de Ph. T. 35, 36, 37, 38, and 39.) Pouillet, in particular, has demonstrated that the gas arising from the surface of burning charcoal is positive, while the charcoal itself is negative; and he has proved that similar phenomena are produced by the combustion of hydrogen, alcohol, oil, and other inflammables of the same kind. In all these instances the combustible, in the act of burning, renders contiguous particles negative; while the oxygen imparts positive electricity to the products of combustion. The fact, with respect to charcoal, was originally noticed by Volta, La Place, and Lavoisier, but was subsequently denied by Saussure and Sir H. Davy. Pouillet has reconciled these conflicting statements by showing that the result depends on the mode in which the experiment is conducted. For if the carbonic acid be completely removed from the burning mass at the instant of its formation, both are found to be electrical; but if the carbonic acid subsequently flow over the surface of the charcoal, the equilibrium will instantly be restored, and no sign whatever of excitement be perceptible. Decisive evidence of the same kind is supplied by the amalgam of the electrical machine, the influence of which is proportional to the degree of chemical action, and which ceases to be useful as soon as the metals are oxidized. Thus, Wollaston found that amalgams of silver and platinum, which are indisposed to oxidize, are of no use when applied to the rubber; and that an amalgam of zinc and tin, which is the most oxidable, is also the best amalgam for exciting the machine. He observed that a machine in good action ceased to act when surrounded with carbonic acid, but instantly recovered its action on readmitting the air. (Phil. Trans. 1801.) On such facts is founded the foregoing statement, that the energy of the electrical machine is much more owing to chemical action than to friction.

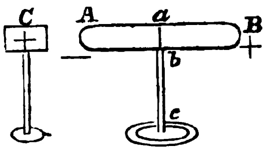
Contact.—Another reputed source of electricity is contact of different substances, especially of metals; a source originally suggested by Volta, who founded on it a theory of galvanism. The facts on which Volta rested his opinion were of this nature. Well-cleaned plates of zinc and copper were furnished with glass handles, by which they could be both supported and insulated: the zinc plate, held by its glass handle, was laid repeatedly on the copper, which at the time need not be insulated, and after each contact the zinc was made to touch the instrument, shortly to be described, called the *condenser*. A positive charge was gradually accumulated; and on operating in the same manner with the insulated plate of copper, it was found to communicate a negative charge. He also stated that if one end of a zinc plate communicate with the condenser, while the zinc at its other end is in contact with a plate of copper, a positive charge is communicated; and that negative electricity is indicated when a copper plate, in contact with zinc at one end, rests at its other upon the condenser. From such experiments it was inferred, that the contact of zinc and copper disturbs the electric equilibrium in both metals, the latter acquiring an excess of negative and the former of positive electricity.

The quantity of electricity developed by contact is confessedly so small, that it requires for its detection the aid of very delicate instruments and of very careful manipulation; and the opinion is daily gaining ground that mere contact is incapable of causing electric excitation. The phenomena referred by Volta to contact, are ascribed by others to chemical action and to friction. De la Rive of Geneva contends (An. de Ch. et de Ph. xxxix. 297,) that the feeble charge commonly observed from the contact of zinc and copper, is due to slight oxidation caused by moisture and oxygen of the air acting on the plate of zinc. When he prevented such oxidation by operating in an atmosphere of hydrogen or nitrogen, no electric excitement followed; and when he purposely increased chemical action, as by exposing the zinc to acid fumes, or by substituting for zinc a more oxidable metal, such as potassium, the electrical effects observable on contact with copper were greatly augmented. Electric excitation and chemical action were observed to be strictly proportional to each other. Again, Parrot of St. Petersburgh (An. de Ch. et de Ph. xlvi. 361,) not only confirms the statements of De la Rive, but shows that in those instances where electric excitement has been witnessed under circumstances which appear to exclude chemical action, the phenomenon may be ascribed to friction of the metals. He gives as the result of numerous experiments made with strict care, that the contact of zinc and copper, if unattended by friction or chemical action, causes not the least developement of electricity. The opposite evidence adduced by Volta and others must, therefore, I apprehend, be rejected; and the only remaining facts in favour of Volta's opinion are derived from certain chemical agencies evinced by metals during contact, a subject which will be discussed in the section on galvanism.

Changes of Form.—The changes of form caused in a substance by variations of temperature, such as liquefaction and solidification, the formation and condensation of vapour, constitute another reputed source of electricity. On liquefying sulphur in a glass vessel, and removing the cake after cooling, the sulphur is found to be negative and the glass positive; and on pouring water into a hot iron vessel or on a hot coal communicating with a delicate electrometer, the rapid evaporation of the water is attended with decisive indications of electrical excitement. To processes of this nature, continually taking place in the atmosphere, the electricity of the clouds is generally ascribed. But the opinion is questioned by Pouillet, who has shown that in most of the experiments adduced in its favour, chemical actions ensue at the same time, and that the greatest part of the effect is due to such changes. If, for example, evaporation be accompanied by chemical decomposition, as when saline solutions are evaporated, the water being separated from the salt with which it was previously united, or if the vessel consist of iron or other easily oxidable material, which is more or less chemically attacked by the evaporating water, then the development of electricity is very decisive; but he contends that pure water, evaporated in a clean platinum vessel, gives rise to no electrical excitement whatever. From such experiments Pouillet concludes that the electricity, hitherto referred to changes of form, is entirely owing to the chemical action by which they are generally attended; and these phenomena, of which evaporation from the ocean, rivers, and the surface of the earth, affords an instance, pure water being thereby separated from its saline impregnation, as also the chemical changes attendant on the growth and nutrition of plants, he regards as a fertile source of atmospheric electricity. (An. de Ch. et de Ph. xxxv. 401, and xxxvi. 5. In these views there is much truth. I have repeatedly noticed free electric excitement on pouring a solution of chloride of sodium or sulphate of soda into a heated platinum crucible, and also when pure water was dropped on red-hot iron or a glowing cinder; but I have as constantly failed of procuring any indication when pure water was evaporating on platinum. Mr. Harris, however, informs me that with an apparatus of unusual delicacy, he finds evaporation of pure water from platinum to be attended with distinct development of electricity.

Proximity to an Electrified Body.—It is a direct consequence of the attractive and repulsive powers ascribed to the electric fluids, that an unelectrified conductor must be excited by the vicinity of an electrified body. Let

Fig. 1.



AB, fig. 1, be an unexcited conductor, supported on an insulating glass rod *bc*; and let C, containing free positive electricity, and similarly insulated, be placed near it on the side A. The free positive electricity on C will both repel the positive fluid of AB, and attract its negative fluid, and the result of these concurring forces is instantly to decompose a portion of the combined electricities of AB, the free negative fluid approaching as close as possible to C, and the positive fluid receding from it. The relative position of these fluids is indicated in the figure by the signs + and —, the former denoting positive and the latter negative electricity. The opposite ends of the conductor AB are thus oppositely electrified, and in an equal degree: the excitement is found, as would be anticipated, to be greatest at the extremities, and to diminish gradually towards the middle line *ab*, which is neutral. The quantity of electricity thus set free depends on the extent to which C is excited, and on its distance from AB. If now C be suddenly withdrawn, the opposite fluids at A and B coalesce, and the equilibrium of AB is restored. But so long as C retains its position, A will be negative, even were it uninsulated. The only effect of communication with the ground is to neutralise the positive fluid at B by supplying to it negative electricity from the earth: if after having effected this by touching the cylinder for an instant with the finger, C be withdrawn, AB is left with an excess of the negative fluid.—The electricity thus developed by the contiguity of an electrified body is said to be *induced*, or to be excited by *induction*.

It is essential that the student should reflect carefully on these plain consequences of the theory of electricity, since the applications of this knowledge are numerous. A few of these may now be enumerated:—

1. An electrified body attracts light objects near it, because it induces in them a state opposite to itself. The attraction is most lively when the light object is a conductor, and in contact with the ground, since it then more completely assumes an electric state opposed to that of the inducing body. A non-conductor is very inperfectly electrified by induction, because the electric fluids cannot quit each other from inability to move through the non-conductor.

2. If a stick of sealing-wax, strongly negative, be presented to a thread or pith ball which is also negatively, but feebly, excited, repulsion will ensue at a considerable distance, followed by attraction when the distance is small. This attraction is due to the strongly excited wax acting by induction on the feebly negative thread, thereby causing it to have an excess of positive electricity.

3. The positive electricity collected on the prime conductor of an electrical machine is by some ascribed, not to a transfer of that fluid from the glass to the prime conductor, but to a part of the combined electricities of the prime conductor being separated by induction, and the negative fluid being imparted to the positive glass. The same view is applicable to any system of conductors in contact with the prime conductor, as also to conductors connected with the rubber. It is difficult to say which explanation is the more correct, or whether both may not be true.

4. On moving the hand towards the prime conductor of an excited electrical machine, the hand becomes negative by induction, and the spark ultimately obtained restores the equilibrium. In like manner a negatively electrified cloud renders positive a contiguous tree or tower, and then a stroke of lightning follows as a consequence of attraction between the two accumulated fluids.

5. The action of the *Leyden Jar* depends on the principle of induced electricity. A glass jar or bottle with a wide mouth is coated externally and internally with tinfoil, except to within three or four inches of its summit; and its aperture is closed by dry wood or some imperfect conductor,

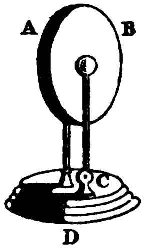
through the centre of which passes a metallic rod communicating with the tinfoil on the inside of the jar. On placing the metallic rod in contact with the prime conductor of an excited electrical machine, while the outer coating communicates with the ground, the interior of the jar acquires a charge of positive electricity, and the exterior becomes as strongly negative. If, the jar being insulated, the metallic rod be placed close to the prime conductor, avoiding actual contact, while an uninsulated conductor be held at an equal distance from the outer coating, electric sparks in equal number and of equal size will pass between both intervals, and both sides of the jar are found to be in the same condition as before; but no charge will be received when the inner coating communicates with the prime conductor, and the outer coating is strictly insulated. From these facts it is inferred that the interior of the jar becomes positive, either by receiving positive electricity directly from the prime conductor, or, as is more probable, by communicating to it negative electricity; and that the exterior then becomes negative by the loss of a quantity of positive electricity equal to that on the interior. Unless means be afforded for the escape of the positive electricity from the exterior, no charge ought to be received; and this conclusion is quite conformable to the fact above stated.

The opposite electric fluids accumulated on the opposite sides of a charged Leyden jar exert a strong mutual attraction through the substance of the glass, and the presence of each secures the continuance of the other. The exterior of the jar may be freely handled, and its coating removed, without destroying the charge, provided no communication be made at the same time with the interior; and if the exterior be insulated, the charge will be preserved, though the tinfoil of the interior be removed. But when a conductor communicates with both surfaces at the same instant, the two fluids rush together with violence, and the equilibrium is restored. Whether in this and similar cases the two fluids coalesce entirely on the intermediate conductor, or whether each from its velocity may not in part pass the other, and be projected to the opposite surface, is a question on which electricians are not agreed.

The Leyden jar affords the means of passing through bodies a large quantity of electricity. For not only may jars of any required size be employed, but it is easy so to arrange any number of such jars, that they shall all be charged and discharged at the same time, constituting what is termed an *Electrical Battery*. The arrangement is made by placing a number of Leyden jars in a box lined with tinfoil, by which means their outer surfaces have free metallic communication with each other, and connecting their inner surfaces by wires.

The explanation above given of the action of a Leyden jar suggests a curious point of theory. A jar after it has been discharged contains a smaller quantity of the combined fluids than before it was charged; since the act of charging is ascribed to loss of negative electricity by the inner and of positive electricity by the outer surface of the jar, which loss is not restored at the moment of discharge. Hence, if the same jar were charged and discharged many times in succession, the total quantity of electricity remaining in the jar ought to be diminished: and yet a Leyden jar does not seem to be impaired by use, but is equally effective at last as at first. Several kinds of assumption may be made to explain this. 1. It is possible that the quantity of electricity present in bodies may be so enormous, that any loss obtained in our experiments is inappreciable. 2. There may be some unknown mode by which electricity abstracted from a substance is restored to it. 3. It may be assumed that when the total quantity of the electricity in a jar is diminished to a certain extent, the excited prime conductor no longer charges the interior by decomposing its combined fluids, but by imparting to it positive electricity; and that the outer surface of the jar is then supplied with a corresponding quantity of electricity directly from the earth.

Fig. 2.



6. The principle of induced electricity was ingeniously applied by Volta in the construction of the *Condenser*. This apparatus, shown in fig. 2, consists of two brass plates, A and B, supported on a common stand D. One of the plates B is attached to the stand by means of a hinge C, so that, though represented upright, it may be placed horizontally, and thus be withdrawn from the vicinity of the plate A, the support of which is made of glass. On electrifying the insulated plate positively, the plate B, expressly placed close to A, is rendered negative by induction; and, as happens in the Leyden jar, the excitement of B will be proportional to that of A. The negative charge of B tends to preserve the positive charge of A, which may consequently receive still more electricity by contact with any positive surface, without losing what it had previously acquired. Thus is electricity accumulated or *condensed* on A; so that a substance too feebly excited to produce any appreciable effects of itself, may, by repeated contact with the insulated plate of a condenser, communicate a charge of considerable intensity. The effect of the accumulation is made apparent by withdrawing B, and bringing A in contact with a delicate electrometer. The condenser is much employed in experiments of delicacy, and the plate A is often permanently fixed on the gold-leaf electrometer.

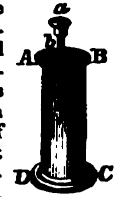
7. The *Electrophorus* is another contrivance of Volta's, which acts by induced electricity. It consists essentially of two parts; one being a flat cake of resin, made by pouring melted resin into a shallow plate or circular dish of tinned iron, and the other a disk of brass, of rather smaller diameter than the resin, supplied with a glass handle. The surface of the resin is negatively excited by friction or flapping with silk or flannel, and the brass disk is laid upon it. The resin being a non-conductor retains its own electricity in spite of the super-imposed brass, and decomposes the combined electricities of the latter, causing its under surface to be positive, and its upper negative. On touching the brass with the finger, its upper surface is neutralized, and on then withdrawing the brass plate, it is found to have an excess of positive electricity. On replacing the brass as before, the resin, having lost none of its electricity in the process, acts again upon the metallic disk as on the first occasion, and will continue so to act for an indefinite number of times. Kept in a dry place the electrophorus will keep in action for months.

ELECTROSCOPES AND ELECTROMETERS.

It is very important, in experiments on electricity, to possess easy methods of discovering when a substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The means for effecting these objects are founded on electrical attraction and repulsion, and the instruments employed for the purpose are called *Electroscopes* and *Electrometers*, the latter denoting the intensity of electricity, the former merely indicating excitement, and the electrical state by which it is produced. The term electrometer, however, is often indiscriminately applied to all such instruments, since the methods of ascertaining the kind of excitement give at the same time some idea of its intensity.

Gold-leaf Electrometer.—Several simple electroscopic methods have already been indicated. (Page 72.) Small balls made of the pith of elder are used for the same purpose. A single pith ball, suspended by a cotton thread, is attracted by a feebly electrified substance. Also, when two pith balls are suspended from the same point by cotton threads of equal length, and an electrified body is placed near them, the two balls are thrown by induction into the same electric state, and diverge. The gold-leaf electrometer, figure 3, invented by Mr. Bennett, acts upon the same principle, but is far more delicate. It consists of a glass cylinder cemented below upon a brass plate CD, and covered above by a brass plate AB, pierced in its centre for the insertion of a glass tube *bc*, the top of which is closed by a brass plate *a*: into this plate is screwed a thick brass wire, which passes through the glass tube, and from the lower end *d* of which two slips of gold-leaf are suspended. These different parts are put together while quite dry, all the joinings are secured by wax cement, and the glass is covered by lac varnish.

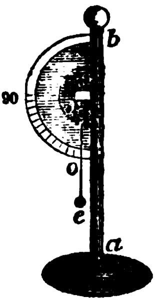
Fig. 3.



The effect of these arrangements is to insulate the plate *a* with its wire and gold leaves, while the latter are secure against being moved by currents of air. The approach of any electrified body, even though feebly excited, to the plate *a*, is immediately detected by the divergence of the leaves, as shown in the figure. The instrument is equally useful in indicating the kind of excitement, provided the plate and leaves be permanently electrified, which may easily be done on the same principle as in charging the metallic disk of an electrophorus. Thus, on placing a negatively excited body, as for example a stick of sealing-wax after friction on woollen cloth, near the brass plate of the electrometer, the electric equilibrium of its whole metallic surface is disturbed: the brass plate becomes positive, and the slips of gold-leaf diverge from being negative. If the plate be then touched with the finger, the equilibrium of the gold-leaves is restored, and their divergence ceases, while an excess of positive electricity is preserved on the plate by the vicinity of the negative sealing-wax. On removing *first* the finger, and *then* the sealing-wax, the brass is left with an excess of positive electricity, which extends over the whole metallic surface of the electrometer, and thus produces a divergence which continues for a considerable time if the glass be dry, and the atmosphere moderately free from moisture. The approach to the brass plate of a positively excited body increases the divergence of the gold leaves; because the plate becomes negative by induction, and the positive fluid retiring to the extremities of the leaves, renders them still more positive. A negatively excited body has an exactly opposite effect, by attracting the positive fluid towards the plate and from the leaves, and diminishing divergence.

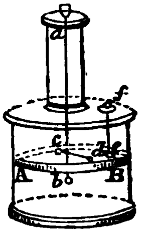
Quadrant Electrometer.—An instrument much used for estimating the degree or intensity of electricity is the *quadrant electrometer*, figure 4, invented by Mr. Henley. It consists of a smooth round stem of wood *a b*, about seven inches long, to the upper part of which, and projecting from its side, is attached a semicircular piece of ivory. In the centre *c* of the semicircle is fixed a pin, from which is suspended, to serve as an index, a slender piece of wood or cane *d e*, four inches in length, and terminated by a small ball. When the apparatus is screwed on the prime conductor of the electrical machine, or placed on any electrified body, it indicates differences of electric intensity by the extent to which the index recedes from the stem; and in order to express the divergence in numbers, the lower half of the semicircle, which is traversed by the index, is divided into 90 equal parts called *degrees*. This instrument, though convenient for experiments of illustration, is not suited to those of research, wherein the object is to examine the effects of substances feebly electrified, and ascertain their relative forces with accuracy.

Fig. 4.



Torsion Electrometer.—This instrument, invented by Coulomb, is peculiarly fitted for scientific investigation. It consists of a small needle of gum-

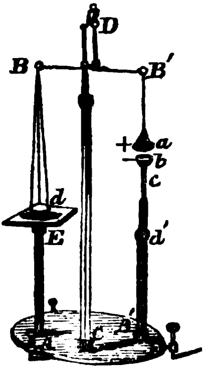
Fig. 5.



lac *c d*, fig. 5, suspended horizontally by a silk thread as spun by the silk-worm, or by a fine silver wire *a b*; on the point of the needle is fixed a small gilt ball made of the pith of elder; and the whole is covered with a glass case to protect it from moisture and currents of air. The pith ball, when the apparatus is at rest, is in contact with the knob *e* of a metallic conductor *fe*, which passes through a hole in the glass case, and is secured in its place by cement; but when an excited body is made to touch the conductor, the pith ball in contact with it is similarly excited, and recedes from it to an extent proportional to the degree of excitement. The needle consequently describes the arc of a circle, which is measured on the graduated arc AB, and in its revolution twists the supporting thread more or less according to the length of the arc described. The torsion thus occasioned calls into play the elasticity of the thread,—a feeble but constant force, which opposes the movement of the needle, measures by the extent to which it is overcome the repulsive force exerted, and brings back the needle to its original position as soon as the electric equilibrium is restored. It has been proved that the force which causes the torsion is exactly proportional to the arc described by the needle.

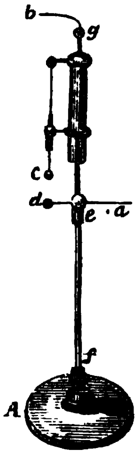
Balance Electrometer.—Mr. Harris of Plymouth has made a happy application of the common balance and weights to estimate the mutual attraction of oppositely electrified surfaces. The apparatus, figure 6, consists of a brass beam BB′, supported by a conductor CD standing on a wooden frame AA′; *d* is a scale for holding weights, and E its support; *a*, *b*, are gilt cones made of light wood, *a* being suspended by a silver wire from B′, and *b* insulated by the glass support A′*d*′. The instrument is prepared for use by placing *a* and *d* in exact equipoise; the cone *a* is suspended so that its base shall be opposite and parallel to the base of the cone *b*, as may be done by means of three adjusting screws in the frame AA′; and *b* is raised by help of a graduated brass slide *c*, until the bases of the cones are just in contact. The cone *b* is then depressed to any desired distance, which may be varied at will during an experiment. The same cone is connected with the inner coating of a Leyden jar, the outer coating of which communicates with the frame of AA′, and along CDB′ with the cone *a*: these cones may thus be made parts of a charged Leyden jar, and be oppositely excited, as indicated by the signs + and —. The attractive forces exerted between their bases tends to draw down the cone *a* into contact with *b*, discharging the jar; but before it can do so, it has to overcome the weight which may be in the scale *d*. By this ingenious contrivance any number of attractive forces are estimated by a common standard, namely, the number of grains which each is able to raise.

Fig. 6.



Unit Jar.—This is another contrivance of Mr. Harris, and is a most important addition to our stock of electrical apparatus. It is formed of a small inverted Leyden jar, figure 7, supported and insulated by a slender glass rod *ef*, which is covered with lac varnish, and fixed into a wooden frame A. The inner coating of this jar is in metallic contact with a brass ball *d* and a wire *a*, which wire communicates with the prime conductor of an active electrical machine; whereas the brass ball *c* and wire *b* are connected with its outer coating. If the wire *b* be held in the hand, or otherwise communicate, with the ground, the electrical machine being in action, the jar is charged in the usual manner, and is discharged by a

Fig. 7.



spark passing between the two brass balls *c* and *d*. The interval may be increased or diminished by causing one of the balls to be moveable by means of a slide or screw. It will be readily conceived that successive sparks through the same interval must be caused by equal quantities of electricity; and experiment shows this to be the case, provided the apparatus is clean and dry, and the charges are taken nearly at the same time, that is, while the air in relation to temperature, pressure, and moisture, may be considered constant. On taking six successive sparks we employ six times as much electricity as for one charge, and three times as much as for two charges, the quantity of electricity being proportional to the number of charges. It is on this account Mr. Harris introduced the term unit jar.

The principal use of the unit jar is in charging other Leyden jars with known proportions of electricity. Thus, if the unit jar be charged by the prime conductor, while its outside communicates through the wire *b* with the inside of a large Leyden jar standing on the ground, the positive fluid repelled from the unit jar gives an equal positive charge to the inner coating of the large jar, and its outer coating is rendered negative by induction. Under these circumstances the effect of a spark between *c* and *d* is merely to neutralize the coatings of the unit jar, without affecting the state of the large jar. On giving a second charge to the unit jar, the large jar receives an increment equal to what it received from the first charge, and the second spark merely restores the equilibrium of the unit jar as before. A third and fourth charges of the unit jar act on the same principle; and, by continuing the process, any known proportions may be given. If the opposite coatings of a jar so charged be connected with the cones of the balance electrometer previously described, the attractive forces due to known relative quantities of electricity may be precisely determined.

Electric Intensity.—Before concluding this account of electrometers, it will be useful to refer to the kind of information which they supply. From the mode in which these instruments act, it is plain that they indicate the *degree* of electric excitement, the remoteness from the unexcited state, a condition expressed by the terms *tension* and *intensity*. If two insulated brass disks of equal size be supplied with equal quantities of free electricity, they will affect an electrometer equally, and, therefore, their intensity or tension is equal; but if one of the disks be larger than the other, the smaller will have the highest tension. In fact, one square inch of the smaller disk will possess more free electricity than the larger, and that is precisely the condition which constitutes differences of intensity. Of any number of electrified substances, that will have the highest intensity which has the most free electric fluid on unity of surface.

LAWS OF ELECTRICAL ACCUMULATION.

1. The quantity of free electricity which an insulated conductor is capable of receiving is independent of its quantity of matter. Thus, two brass spheres of the same size, one solid and the other hollow, will take equal quantities of electricity, and possess equal intensities. The cause of this is referable to the second law.

2. The free electricity of an insulated conductor is always accumulated on its surface, where it forms a layer or stratum enveloping the substance on every side, and, therefore, possessed of the same figure. Thus, an excited sphere, the surface of which is exactly fitted with two thin metallic hemispheres, loses the whole charge, when, by means of glass handles, the hemispheres are suddenly removed; and an excited hollow cylinder, open at

the ends, will admit of being touched by an insulated conductor, cautiously introduced into its interior, without any loss of electricity. The cause of free electricity being disposed upon the surface of conductors is ascribed to the mutual repulsion of its particles, which gives them a tendency to recede as far as possible from each other, and to be arrested at the surface solely by some counteracting force, such as the interposition of an imperfect conductor.

3. The mode in which electricity is distributed over the surface of a conductor is dependent on its figure. On a sphere it forms a uniform stratum of equal thickness all around, that is, each part of the surface has the same quantity of electricity as any other part of equal size. But on an ellipsoid the stratum is thickest at the extremities of the longer axis, and the accumulation at those parts is greater and greater as the length of that axis becomes more and more predominant. In all conductors which are much longer than broad, as in a narrow metallic bar, as also in those which have elongated pointed terminations, the principal accumulation is at the ends and projecting points. The inequality of distribution is just as conspicuous in a negatively as in a positively excited conductor, a circumstance which seems utterly irreconcilable with the theory of a single fluid. Coulomb proved these facts experimentally by touching the different parts of electrified conductors by a *proof-plane*, which is a very small disk of gilt paper insulated by a handle of lac resin, and estimating the tension of the proof-plane by his torsion electrometer: he found that this plane always took from the spot touched a constant proportion of the electricity accumulated at that spot, and, therefore, the relative intensities of the plane, after contact with different parts of an electrified conductor, exactly represented the electric accumulation of the parts so touched. For these and other experiments of Coulomb on electrical actions, the reader may consult Biot's *Traité de Physique*.

The unequal accumulation of electricity on conductors is a direct consequence of the law of electric repulsion; and M. Poisson, assuming the truth of that law, has arrived by calculation at the very same conclusions which Coulomb obtained by experiment. Those who are prepared to follow such very high mathematical inquiries are referred to Poisson's original Essay, to the article on Electricity by Mr. Whewell in the Encyclopedia Metropolitana, and to a late work on Electricity by Mr. Murphy.

4. The electric fluid accumulated at the surface of conductors tends to escape by the repulsion of its particles. Its pressure against the air is considered proportional to the square of the quantity; so that if the electric accumulation at four different parts of an excited conductor is as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. Hence electricity passes off with great rapidity from the ends or projecting points of conductors, a result quite conformable to experience. But the equilibrium of an excited conductor is perhaps never entirely restored by the direct diffusion of its excess due to its own repulsion; for the conductor necessarily tends to induce a state opposite to itself in contiguous conductors and in the circumambient air, and then the attraction of oppositely electrified surfaces is called into play.

5. Coulomb proved experimentally, by aid of his torsion electrometer, that the repulsion of two similarly electrified bodies varies inversely as the square of their distances. If the electric charge on one of them vary, while that on the other and the distance are constant, the repulsion will vary simply as the quantity. Thus, let the free electricity on A be expressed by 4, and that on B by 1, and the distance be always 1 inch, then if the charges on B vary as 1, 2, 3, and 4, the repulsion will also vary as 1, 2, 3, and 4; for the successive additions to B merely act by augmenting in the same ratio the number of repulsive particles influenced by the constant charge on A. The repulsion in these cases may be denoted by the product of the two charges. For example, when the charges on A and B are 4 and 1, the repulsion will be $4 \times 1 = 4$; when they are 4 and 2, the repulsion is $4 \times 2 = 8$, or twice four;

when 4 and 3, it is 4×3=12, or three times four; and when 4 and 4, the repulsion is 4×4=16, or four times four. If in the last case the charge on B fall to 2, the repulsion becomes 4×2=8 as before; and then should the charge on A be also reduced to 2, the repulsion will be 2×2=4. Hence when the *whole* quantity of electricity changes, the repulsion varies as the square of the quantity.

6. The attraction of two oppositely electrified bodies varies inversely as the square of the distance between them. Coulomb, who verified this law by experiment, also showed that the attractive force, the distance being constant, varies by the same law as that for repulsion just stated. If A and B are equally and oppositely excited, so that we may represent the free electricity on each by 4, and their mutual attraction by 4×4=16, then if the quantity on B successively become 3, 2, and 1, the corresponding attractions will be 12, 8, 4; and should the quantity on A and on B vary together, so as to be reduced on both from 4 to 2, and from 2 to 1, the attractions will be 16, 4, and 1. Thus, when the *whole* quantity of electricity changes, the attraction varies as the square of the quantity.

Mr. Harris has given a beautiful demonstration of these laws by means of his balance electrometer and unit jar (pages 82, 83), the cones *a*, *b*, of figure 6, being connected respectively with the outer and inner coatings of a large Leyden jar. On giving to it a constant charge by means of the unit jar, and varying the distance, the weights raised, or the attractive force, were found to vary exactly as the square of the distance between the cones. On preserving the distance constant, giving a charge capable of raising one grain, and then successively doubling, trebling, and quadrupling the quantity first given to the inner coating, the weights raised were 4, 9, and 16 grains. This strictly conforms with the foregoing statement; for on doubling the charge to the inner coating of the Leyden jar, the electricity on the cone *b*, connected with it, is also doubled, and the double charge on *b* doubles the induced charge on *a*. Hence the quantity on both cones being doubled, the force ought to be quadrupled.

7. It may be inferred from the law No. 6, that when, in two oppositely excited bodies, the whole quantity of electricity and the distance vary together and at the same rate, the attractive force will be unchanged. This has been fully proved by Mr. Harris. On putting 5 grains into his balance, giving a charge sufficient to raise that weight at a certain distance, and then successively doubling, trebling, and quadrupling that distance, it will be necessary, in order to raise the 5 grains, to give a double, treble, and quadruple charge to the inner coating of the Leyden jar communicating with cone *b*. In fact, doubling the electricity on both cones, is to quadruple the attractive force between them; and doubling the distance, diminishes the force by four times: the force is thus diminished by one cause as much as it is increased by the other, and, therefore, continues unchanged.

Mr. Harris has demonstrated the same law by observing the *striking distance* of a charged jar, that is, the interval through which the electricity will pass so as to discharge it. For this purpose the inner and outer coating are separately connected with a conductor terminating in a brass ball, one of which is attached to a graduated slide, so as to be fixed at any required distance from the other ball. On causing the distances between the balls to vary in the ratio of 1, 2, 3, 4, the jar will discharge itself by the passage of a spark, when the charge on each coating is increased in the same ratio. The obstacle which the electricity has to overcome before it can discharge the jar, is the interposed air; and that obstacle may be regarded as constant in experiments performed at the same time, since it is found to depend on the density of the air.

8. Mr. Harris ascertained the nature of the influence exerted by the atmosphere over the striking distance of a charged Leyden jar, by including the balls connected with its outer and inner coating within glass vessels susceptible of exhaustion. He then found that the resistance to the passage of a charge varies as the square of the density of the air. Thus, when the den-

sity was made to vary in the ratio of 1, 2, 4, the charge passed through a constant interval when the quantity added to the inner coating varied in the same ratio. Now, when the charges were as 1, 2, 4, the attractive forces, by law No. 6, were as 1, 4, 16, which represent the corresponding obstacles caused by the air. Agreeably to the same law, the striking distance, when the charge is constant, varies inversely as the density of the air: a charge which strikes through one inch of air when the barometer is at 30 inches, will pass through two inches in air so rarefied as to support only 15 inches of mercury, and through four inches when the mercurial column is 7.5 inches. Hence, in a perfect vacuum, a Leyden jar ought to discharge itself through any interval; and in the higher parts of the atmosphere, where the air is much rarefied, two oppositely-excited clouds will neutralize each other, though separated by very great distances.

It is not apparent from the preceding remarks, whether the striking distance is influenced by change of the density or the elasticity of the confined air, since in rarefying air by the air-pump, the rarefaction increases, and the elasticity decreases at the same rate. Mr. Harris has shown, contrary to what one might anticipate, that the influential condition is density and not elasticity. For on rarefying air by heat so as to preserve its original elasticity, the striking distance was exactly the same as in cold air rarefied to the same degree by the air-pump; and in air first rarefied by the air-pump, and then heated until it had recovered its original elasticity, its volume and density being kept the same, the varied elasticity had no influence on the charge required to pass through a constant distance. From these and similar experiments Mr. Harris infers that the remarkable conducting power known to be possessed by hot air is due to its rarity alone.—Though I have not had occasion to repeat these experiments on hot air, I have entire confidence in their accuracy; inasmuch as, not to mention the known skill and exactness of Mr. Harris, I find that the striking distance for the same charge is greater in air than in carbonic acid gas, and greater in hydrogen gas than in air, the elasticities being equal.

9. The continuance of an excited charge on an insulated conductor is commonly ascribed to the pressure of the air. An opposite opinion, however, has been maintained. Mr. Morgan (Phil. Trans. 1785) published some experiments to prove that a space entirely free from air, such as a Torricellian vacuum, is a non-conductor of electricity; and Mr. Cavallo (Treatise on Electricity) showed that exhaustion may be carried very far within the bell-jar of an air-pump without an electrified body placed under it losing its charge. On repeating these experiments, at the request of Mr. Harris, I obtained similar results. A slip of gold-leaf diverging at an angle of 60°, continued so for hours in air expanded 100 times; and in air rarefied 300 times a feeble charge was retained for a whole week. The loss observed in still further states of exhaustion, may be ascribed to the excited body inducing an opposite state in the conducting materials of the air-pump, thereby calling into activity a force which co-operates with the repulsion of its own particles. The preceding phenomena appear to indicate the existence of an adhesive force between the particles of electricity and the surface of bodies which causes an obstacle to their escape.

The facts which I have given in the few preceding pages on the authority of Mr. Harris, are described by him at length in an essay just read before the Royal Society. Owing to his kindness in procuring for me his apparatus, and showing me his method of operating, I have been enabled to repeat all the experiments referred to, except those on heated air, and am quite satisfied of their accuracy.

HISTORICAL NOTICE.

The science of electricity is of modern origin. The knowledge of the ancients was confined to the fact, that amber and the *lyncurium* (supposed to be tourmalin) acquired the property of attracting light bodies by friction. It was not known that other bodies might be similarly excited until the commencement of the seventeenth century, when Dr. Gilbert of Colchester detected the same property in a variety of other substances, and thereby laid the foundation of the science of electricity. A few additional facts were noticed during the same century by Boyle, Otto de Guericke, and Wall, and in 1709 Hawkesbee published an account of many curious electrical experiments; but no material progress was made until Stephen Grey (Phil. Trans. 1729 to 1733) drew the distinction between conductors and non-conductors of electricity, and illustrated it by new and striking experiments. Soon after Dufay in France distinguished between the two kinds of electricity; and in 1759 (Phil. Trans. li. 340) Symmer added the important fact that friction developes both kinds of electricity at the same time, an observation which led to the theory of two electric fluids as now understood. These discoveries added to the confirmation of Franklin's opinion as to the identity of the cause of lightning and electricity, fixed the attention of scientific men upon the new study, and soon acquired for it a high rank among the sciences.

For further details respecting its origin and early progress, the reader may consult the history of electricity by Priestley.

SECTION IV.

GALVANISM.

The science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena are owing to electricity present in the muscles, and that the metals only serve the purpose of a conductor. He conceived that the animal electricity originates in the brain, is distributed to every part of the system, and resides particularly in the muscles. He was of opinion that the different parts of each muscular fibril are in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions take place whenever the electric equilibrium is restored. This he supposed to be effected during life through the medium of the nerves, and to have been produced in his experiments by the intervention of metallic conductors.

The views of Galvani had several opponents, one of whom, the celebrated Volta, Professor of Natural Philosophy at Pavia, succeeded in pointing out their fallacy. Volta maintained that electric excitement is due solely to the metals, and that the muscular contractions are occasioned by the electricity thus developed passing along the nerves and muscles of the animal. To the experiments instituted by Volta, we are indebted for the first voltaic apparatus, which was described by him in the Philosophical Transactions for 1800, and which has properly received the name of the *voltaic pile;* and to the same distinguished philosopher belongs the real merit of laying the foundation of the science of Galvanism.

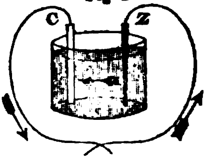
The identity of the agent concerned in the phenomena of galvanism and of the common electrical machine, is now a matter of demonstration. Voltaic and, common elecricity are due to the same force, excited by different conditions, operating in general in a different manner and under different circumstances. The effects of the latter are caused by a comparatively small quantity of electricity brought into a state of insulation, in which state it exerts a high intensity, as evinced by its remarkable attractive and repulsive energies, and by its power to force a passage through obstructing media. In galvanism the electric agent is more intimately associated with other substances, is developed in large quantity, but never attains a high tension, and produces its peculiar effects while flowing along conductors in a continuous current.

VOLTAIC ARRANGEMENTS OR CIRCLES.

Arrangements for exciting galvanism are divided into simple and compound, the former being voltaic circles in their most elementary form, and the latter a collection of simple circles acting together: it will hence be proper to commence the description of them with the most simple.

Simple Voltaic Circles.—When a plate of zinc and a plate of copper are placed in a vessel of water, and the two metals are made to touch each other, either directly or by the intervention of a metallic wire, galvanism is excited. The action is, indeed, very feeble, and not to be detected by ordinary methods; but if a little sulphuric acid be added to the water, numerous globules of hydrogen gas will be evolved at the surface of the copper. This phenomenon continues uninterruptedly while metallic contact between the plates continues, in which state the circuit is said to be *closed;* but it ceases when the circuit is broken, that is when metallic contact is interrupted. The hydrogen gas which arises from the copper plate results from water decomposed by the electric current, and its ceasing to appear indicates the moment when the current ceases. In this case the voltaic circle consists of zinc, copper, and interposed dilute acid; and the circle gives rise to a current only when the two metals are in contact. This arrangement is shown in figure 1, where metallic contact is readily made or broken by means of copper wires soldered to the plates. By employing a galvanometer (page 110), it is found that a current of positive electricity continually circulates in the closed circuit from the zinc through the liquid to the copper, and from the copper along the conducting wires to the zinc, as indicated by the arrows in the figure. A current of negative electricity, agreeably to the theory of two electric fluids, ought to traverse the apparatus in a direction precisely reversed; but for the sake of simplicity I shall hereafter indicate the course of the positive current only.

Fig. 1.



It matters not, so far as voltaic action is concerned, at what part the plates of fig. 1 touch each other. A current takes place, whether contact between the plates is made below where covered with liquid, above where uncovered, or along the whole length of the plates, provided both plates are immersed in the same vessel of dilute acid. Immersion of one plate only in the acid solution, however contact between the plates may be made, does not excite voltaic action; nor does it suffice to have one plate in one vessel, and the other plate in another vessel. A plate of zinc soldered to one of copper, and plunged into dilute acid, gives a current passing from the zinc through the fluid round to the copper: but if the soldered plates are cemented into a box with a wooden bottom and metallic sides, so as to form two *separate* cells, as shown in a vertical section by figure 2, then the introduction of dilute acid to the cells will not excite a current, unless the fluid of the cells be made to communicate by means of moistened fibres of twine, cotton, or some porous matter, or, as in the figure, by wires, *a b*, soldered to the metallic sides which contain the dilute acid, or dipping into the acid itself. Then the positive current circulates in the direction shown by the arrows.

Fig. 2.

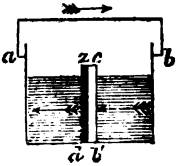
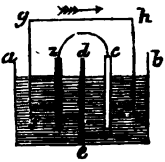
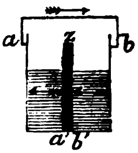


Fig. 3.



Instead of a pair of plates being soldered together, they may be connected by a wire, and plunged into separate cells, *a e*, *b e*, figure 3, in which *d e* acts as a partition; provided the positive current issuing from the zinc plate *z*, is conveyed by a wire, *f g h i*, or some conducting medium, into the cell, *b e*, in which the copper-plate, *c*, is immersed.

Fig. 4.



A simple voltaic circle may be formed of one metal and two liquids, provided the liquids are such that a stronger chemical action is induced on one side than on the other. Thus, on cementing a plate of zinc, *z*, into a box, figure 4, and putting a solution of salt into the cell, *b b′*, and dilute nitric acid into the cell, *a a′*, a positive current will be excited in the direction of the arrows, provided the circuit be completed by a wire, *a b*, attached to the metallic sides of the box, or dipped into the liquid of the cells. Nay, the same acid solution may occupy both cells, provided some condition be introduced which shall cause one side of the zinc to be more rapidly dissolved than the other; as by the plate being rough on one side and polished on the other, or by the acid being hot in one cell and cold in the other. In this case, however, the result is the same as though two different liquids were used.

An interesting kind of simple voltaic circle is afforded by commercial zinc. This metal, as sold in the shops, contains traces of tin and lead, with rather more than one per cent of iron, which is mechanically diffused through its substance: on immersion in dilute sulphuric acid, these small particles of iron and the adjacent zinc form numerous voltaic circles, transmitting their currents through the acid which moistens them, and disengaging a large quantity of hydrogen gas. Pure distilled zinc is very slowly acted on by dilute sulphuric acid of sp. gr. ranging from 1.068 to 1.215; but if fused with about 2 per cent, or rather less, of iron filings, it is as readily dissolved as commercial zinc. In like manner, pure iron or steel is less readily acted on by dilute sulphuric acid than the same substances after fusion with small quantities of platinum or silver. Mr. Sturgeon has remarked that commercial zinc, with its surface amalgamated, which may be done by dipping a zinc plate into nitric acid diluted with two or three parts of water, and then rubbing it with mercury, resists the action of dilute acid fully as well as the purest zinc. This fact, of which Faraday in his late researches has made excellent use, appears due to the mercury bringing the surface of the zinc to a state of perfect uniformity, preventing those differences between one spot and another, which are essential to the production of minute currents; one part has the same tendency to combine with electricity as another, and cannot act as a discharger to it (Faraday).

While the current formed by the contact of two metals gives increased effect to the affinity of one of them for some element of the solution, the ability of the other metal to undergo the same change is proportionally diminished. Thus, when plates of zinc and copper touch each other in dilute acid, the zinc oxidizes more, and the copper less, rapidly than without contact. This principle was beautifully exemplified by the attempt of Davy to preserve the copper sheathing of ships. A sheet of copper immersed in sea-water, or a solution of chloride of sodium, in an open vessel, undergoes rapid corrosion; and a green powder commonly termed submuriate of copper, but which is really an oxy-chloride, is formed: atmospheric oxygen dissolved in sea-water unites both with copper and sodium, the latter yields its chlorine to another portion of copper, and the oxide and chloride of copper unite. But if the copper be in contact with zinc, or some metal more electro-positive than itself, the zinc undergoes the same change as the copper did, and the latter is preserved. Davy found that the quantity of zinc required thus to form an efficient voltaic circle with copper was very small. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve 40 or 50 square inches of copper; and this wherever it was placed; whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connexion between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40 to 1-1000th part of their surface of zinc, malleable and cast iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150th, there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1-1000th part of cast-iron saved a certain proportion of the copper (Phil. Trans. 1824).

Unhappily, for the application of this principle in practice, it is found that unless a certain degree of corrosion takes place in the copper, its surface becomes foul from the adhesion of sea-weeds and shell-fish. The oxy-chloride of copper, formed when the sheathing is unprotected, is probably injurious to these plants and animals, and thus preserves the copper free from foreign bodies.

Simple voltaic circles may be formed of very various materials; but the combinations usually employed consist either of two perfect and one imperfect conductor of electricity, or of one perfect and two imperfect conductors. The substances included under the title of perfect conductors are metals and charcoal, and the imperfect conductors are water and aqueous solutions. It is essential to the operation of the first kind of circle, that the imperfect conductor act chemically on one of the metals; and in case of its attacking both, the action must be greater on one metal than on the other. It is also found generally, if not universally, that the metal most attacked is positive with respect to the other, or bears to it the same relation as zinc to copper in figures 1, 2, and 3. Davy, in his Bakerian lecture for 1826 (Phil. Trans.), gave the following list of the first kind of arrangements, the imperfect conductor being either the common acids, alkaline solutions, or solutions of metallic sulphurets, such as sulphuret of potassium. The metal first mentioned is positive to those standing after it in the series.

With common acids.—Potassium and its amalgams, barium and its amalgams, amalgam of zinc, cadmium, tin, iron, bismuth, antimony, lead, copper, silver, palladium, tellurium, gold, charcoal, platinum, iridium, rhodium.

With alkaline solutions.—The alkaligenous metals and their amalgams, zinc, tin, lead, copper, iron, silver, palladium, gold, and platinum.

With solutions of metallic sulphurets.—Zinc, tin, copper, iron, bismuth, silver, platinum, palladium, gold, charcoal.

Mr. Faraday has shown that the presence of water is not essential. A battery may be composed of other liquid compounds, such as a fused metallic chloride, iodide, or fluoride, provided it is decomposable by galvanism, and acts chemically on one metal of the circle more powerfully than on the other.

The following table of voltaic circles of the second kind is from Davy's Elements of Chemical Philosophy:—

Solution of sulphuret of potassium ——— potassa ——— soda	Copper Silver Lead Tin Zinc Other metals Charcoal	Nitric acid Sulphuric acid Hydrochloric acid Any solutions containing acid.

The most energetic of these combinations is that in which the metal is chemically attacked on one side by sulphuret of potassium, and on the other by an acid. The experiment may be made by pouring dilute nitric acid into a cup of copper or silver, which stands in another vessel containing sulphuret of potassium. The following arrangements may also be employed:—Let two pieces of thick flannel be moistened, one with dilute acid and the other with the sulphuret, and then placed on opposite sides of a plate of copper, completing the circuit by touching each piece of flannel with a conducting wire: or, take two discs of copper, each with its appropriate wire, immerse one disc into a glass filled with dilute acid, and the other into a separate glass with alkaline solution, and connect the two vessels by a few threads of amianthus or cotton moistened with a solution of salt. A similar combination may be disposed in this order: let one disc of copper be placed on a piece of glass or dry wood; on its upper surface lay in succession three pieces of flannel, the first moistened with dilute acid, the second with solution of salt, and the third with sulphuret of potassium, and then cover the last with the other disc of copper.

Metallic bodies are not essential to the production of galvanic phenomena. Combinations have been made with layers of charcoal and plumbago, of slices of muscle and brain, and beet-root and wood; but the force of these circles, though accumulated by the union of numerous pairs, is extremely feeble, and they are very rarely employed in practice.

Of the simple voltaic circles above described, the only one used for ordinary purposes is that composed of a pair of zinc and copper plates excited by an acid solution arranged as in figure 1. The form and size of the apparatus are exceedingly various. Instead of actually immersing the plates in the solution, a piece of moistened cloth may be placed between them. Sometimes the copper plate is made into a cup for containing the liquid, and the zinc is fixed between its two sides, as shown by the accompanying transverse vertical section, figure 5; care being taken to avoid actual contact between the plates, by interposing pieces of wood, cork, or other imperfect conductor of electricity. Another contrivance, which is much more convenient, because the zinc may be removed at will and have its surface cleaned, is that represented by the annexed wood-cut. (Fig. 6.) C is a cup made with two cylinders of sheet copper, of unequal size, placed one within the other, and soldered together at bottom, so as to leave an intermediate space *a a a*, for containing the zinc cylinder *z* and the acid solution. The small copper cups *b b* are useful appendages; for by filling them with mercury, and inserting the ends of a wire, the voltaic circuit may be closed or broken with ease and expedition. This apparatus is very serviceable in experiments on electro-magnetism.

Fig. 5.

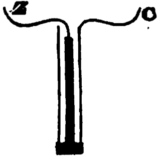
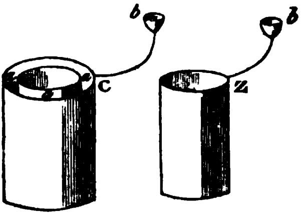


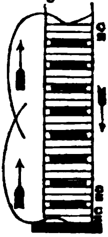
Fig. 6.



Another kind of circle may be formed by coiling a sheet of zinc and copper round each other, so that each surface of the zinc may be opposed to one copper, and separated from it by a small interval. The London Institution possesses a very large apparatus of this sort, made under the direction of Mr. Pepys, each plate of which is 60 feet long and two wide. The plates are prevented from coming into actual contact by interposed ropes of horsehair; and the coil, when used, is lifted by ropes and pulleys, and let down into a tub containing dilute acid. The contrivance of opposing one large connected surface of zinc to a similar surface of copper, originated with Dr. Hare of Philadelphia, who, from its surprising power of igniting metals, gave it the name of *Calorimotor*.

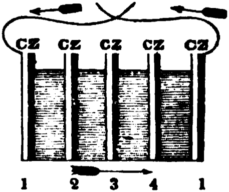
Compound Voltaic Circles.—This expression is applied to voltaic arrangements which consist of a series of simple circles. The first combinations of the kind were described by Volta, and are now well known under the names of *voltaic pile* and *crown of cups*. The voltaic pile is made by placing pairs of zinc and copper, or zinc and silver plates, one above the other, as shown in figure 7, each pair separated from those adjoining by pieces of cloth, rather smaller than the plates, and moistened with a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the zinc be placed below the copper in the first pair, the same order should be observed in all the others. Without such precaution the apparatus would give rise to opposite currents, which would neutralize each other more or less according to their relative forces. The pile, which may consist of any convenient number of combinations, should be contained in a frame formed of glass pillars fixed into a piece of thick dry wood, by which it is both supported and insulated. Any number of these piles may be made to act in concert by establishing metallic communication between the positive extremity of each pile and the negative extremity of the pile immediately following.

Fig. 7.



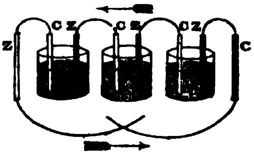
The voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery proposed by Mr. Cruickshank, consists of a trough of baked wood, about 30 inches long, in which are placed at equal distances 50 pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made water-tight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution, which serves the same purpose as the moistened cloth in the pile of Volta. By means of the accompanying wood-cut the mode in which the plates are arranged will easily be understood.

Fig. 8.



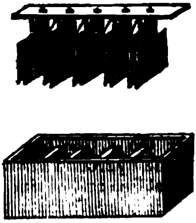
Other modes of combination are now in use, which facilitate the employment of the voltaic apparatus and increase its energy. Most of these may be regarded as modifications of the crown of cups. In this apparatus the exciting solution is contained in separate cups or glasses, disposed circularly or in a line: each glass contains a pair of plates; and each zinc plate is attached to the copper of the next pair by a metallic wire, as represented in figure 9. Instead of glasses, it is more convenient in practice to employ a trough of baked wood or glazed earthenware, divided into separate cells by partitions of the same material; and in order that the plates may be immersed into and taken out of the liquid conveniently and at the same moment, they are all attached to a bar of dry wood, the necessary connexion between

Fig. 9.



the zinc of one cell and the copper of the adjoining one being accomplished, as shown in figure 10, by a slip or wire of copper.

Fig. 10.



A material improvement in the foregoing apparatus was suggested by Dr. Wollaston (Mr. Children's Essay in Phil. Trans. for 1815), who recommended that each cell should contain one zinc and two copper plates, so that both surfaces of the former metal might be opposed to one of the latter. The two copper plates communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one-half the power is said to be obtained by this method.

A variation of this contrivance, which appears to me advantageous, has been suggested by Mr. Hart of Glasgow, who proposes to have the double copper plates of the preceding battery made with sides and bottoms, so that, as in figure 5, they may contain the exciting liquid. The plates are attached, as in figure 10, to a bar of wood, and supported above the ground by vertical columns of the same material, by which they are insulated. The cells are filled by dipping the whole battery into a trough of the same form, full of the exciting liquid. (Brewster's Journal, iv. 19.)

The size and number of the plates may be varied at pleasure. The largest battery ever made is that of Mr. Children, described in the essay above referred to, the plates of which were six feet long, and two feet eight inches broad. The common and most convenient size for the plates is four or six inches square; and when great power is required, a number of different batteries are united by establishing metallic communication between the positive extremity or pole of one battery and the negative pole of the adjoining one. A very effective battery was described by Dr. Hare under the name of the *Deflagrator*, which consisted of 80 zinc plates, 9 inches by 6 in size, and 80 copper plates, 14 inches by 6, coiled together, and so connected that the whole could be immersed into the exciting liquid, or removed from it, at the same instant (An. of Phil. xvii. 329). The great battery of the Royal Institution, with which Davy made his celebrated discovery of the compound nature of the alkalies, was composed of 2000 pairs of plates, each plate having 32 square inches of surface. It is now recognized, however, that such large compound batteries are by no means necessary. Increasing the number of plates beyond a very moderate limit gives, for most purposes, no proportionate increase of power; so that a battery of 50 or 100 pair of plates, thrown into vigorous action, will be just as effective as one of far greater extent.

The electrical condition of compound voltaic arrangements is similar to that of the simple circle. In the broken circuit no electric current can be traced; but in the closed circuit, that is, when the wires from the opposite ends of the battery are in contact, the galvanometer indicates a positive electric current through the battery itself and along the wires, as shown by the arrows in figures 8 and 9. The direction of the current appears at first view to be different from that of the simple circle; since in the latter the positive electric current flows from the zinc through the liquid to the copper, while in the compound circle its direction is from the extreme copper through the battery to the extreme zinc plate. This apparent difference arises from the compound circle being usually terminated by two superfluous plates. The extreme copper and extreme zinc plate of figure 8 are not in contact with the exciting fluid, and therefore contribute nothing to the galvanic action: removing these superfluous plates, which are solely conductors, there will remain four simple circles, namely, the 3 pair of soldered plates marked 2, 3, 4, which act as in figure 2, and the then extreme plates, 1, 1, which are related to each other as the plates in fig. 1. When thus arranged, the direction of the current will be seen to correspond with that of the simple circle.

During the action of a simple circle, as of zinc and copper, excited by dilute sulphuric acid, all of the hydrogen developed in the voltaic process is evolved at the surface of the copper. This fact is not apparent when common zinc plates are used, owing to the numerous currents which form on the surface of the zinc (page 89); but when a plate of amalgamated zinc and another of platinum are introduced into dilute sulphuric acid of sp. gr. 1.068 or a little higher, no gas whatever appears until contact between the plates is made, and then hydrogen gas rises solely from the platinum, while zinc is tranquilly dissolved. On weighing the amalgamated plate before and after the action has continued for half an hour or an hour, and collecting the hydrogen gas evolved during that interval, the weight of the hydrogen set free and of zinc dissolved will be as 1 to 32.3, being the ratio of their chemical equivalents. Mr. Faraday, who has lately proved this, has also shown that in a compound voltaic circle, say of 10 amalgamated zinc plates and 10 of platinum, each of the former during a given period of action loses exactly the same weight, and from each of the latter an equivalent quantity of hydrogen gas is evolved. This separation of one ingredient of the exciting solution at one plate, while the element previously combined with it unites with the other plate, seems essential to voltaic action. It is in some way connected with the passage of the current across the exciting liquid. Oxygen in a free state may, by oxidizing zinc, cause electric excitement; but the voltaic current is not established, unless the oxygen formed part of a previous liquid compound in contact or communication with both the plates.

Among the different kinds of voltaic apparatus is usually placed the electric column of De Luc, which is formed of successive pairs of silver and zinc, or silver and Dutch-metal leaf, separated by pieces of paper, arranged as in a voltaic pile. It is remarkable for its power of exhibiting attractions and repulsions like common electricity, but cannot produce chemical decomposition or any of the effects most characteristic of a voltaic current, and is rather an electrical than a voltaic instrument. It is quoted as a proof of electric development by contact, since it will continue in action for years without being cleaned or taken to pieces. True it is that the more oxidable metal of the column is slowly corroded, and that no electricity is excited when the paper is quite or nearly free from hygrometric moisture, the presence of which is necessary to the oxidation of the zinc and copper; but at the same time the quantity of electricity excited seems so disproportioned to the corrosion, that the one can scarcely be assigned as the cause of the other.

THEORIES OF GALVANISM.

Of the theories proposed to account for the development of electricity in voltaic combinations, three in particular have attracted the notice of philosophers. The first originated with Volta, who conceived that electricity is set in motion, and the supply kept up, solely by contact or communication between the metals (page 87). He regarded the interposed solutions merely as conductors, by means of which the electricity developed by each pair of plates is conveyed from one part of the apparatus to the other. Thus, in the pile or ordinary battery, represented by the following series,

$$+\ \overbrace{\text{zinc copper}}^{3}\ \ \overset{\longleftarrow}{\text{fluid}}\ \ \overbrace{\text{zinc copper}}^{2}\ \ \overset{\longleftarrow}{\text{fluid}}\ \ \overbrace{\text{zinc copper}}^{1}\ -$$

Volta considered that contact between the metals occasions the zinc in each pair to be positive, and the corresponding copper plate to be negative; that the positive zinc in each pair except the last, being separated by an intervening stratum of liquid from the negative copper of the following pair, yields to it its excess of electricity; and that in this way each zinc plate communicates, not only the electricity developed by its own contact with copper, but also that which it had received from the pair of plates immediately before it. Thus, in the three pairs of plates contained in brackets, the second pair receives electricity from the first only, while the third pair draws a supply from the first and second. Hence electricity is most freely accumulated at one end of the battery, and is proportionally deficient at the opposite extremity. The intensity is, therefore, greatest in the extreme pairs, gradually diminishes in approaching the centre, and the central pair itself is neither positively nor negatively excited. In batteries constructed on the principle of the crown of cups (fig. 9), the *electro-motion*, as Volta called it, is ascribed to metallic communication between the zinc of one glass and the copper of the adjoining one.

The second is the *chemical theory*, proposed by Wollaston. Volta attached little importance to the chemical changes which never fail to occur in every voltaic circle, whether simple or compound, considering them as casual or unessential phenomena, and therefore neglected them in the construction of his theory. The constancy of their occurrence, however, soon attracted notice. In the earlier discussions on the cause of spasmodic movements in the frog (page 87), Fabroni contended, in opposition to Volta, that the effect was not owing to electricity at all, but to the stimulus of the metallic oxide formed, or of the heat evolved during its production. More extended researches soon proved the fallacy of this doctrine; but Fabroni made a most ingenious use of the facts within his knowledge, and paved the way to the chemical theory of Wollaston.

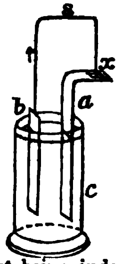
The late Dr. Wollaston, fully admitting electricity as the voltaic agent, assigned chemical action as the cause by which it is excited. The repetition and extension of Volta's experiments by the English chemists, speedily detected the error he had committed in overlooking the chemical phenomena which occur within the pile. It was observed that no sensible effects are produced by a combination of conductors which do not act chemically on each other; that the action of the pile is always accompanied by the oxidation of the zinc; and that the energy of the pile in general is proportional to the activity with which its plates are corroded. Observations of this nature induced Wollaston to conclude that the process begins with the oxidation of the zinc,—that oxidation, or in other terms, chemical action was the primary cause of the development of electricity,—that the fluid of the circle served both to oxidize the zinc and to conduct the electricity which was excited,—and that contact between the plates served only to conduct electricity, and thereby complete the circuit.

The third theory of the pile was proposed by Davy, and is intermediate between the two former. He adduced many experiments in support of the fact originally stated by Volta, that the electric equilibrium is disturbed by the contact of different substances, without any chemical action taking place between them. He acknowledged, however, with Wollaston, that the chemical changes contribute to the general result; and he maintained that, though not the primary movers of the electric current, they are essential to the continued and energetic action of every voltaic circle. The electric excitement was begun, he thought, by metallic contact, and maintained by chemical action.

The progress of inquiry since these theories first came into notice, has gradually given more and more support to the views of Wollaston, and has at last, I apprehend, established it to the entire exclusion of the theory of Volta. The very fundamental position, that electricity is excitable as a primary result by the contact of different substances, is warmly contested, and, as some think with strong reason, has been disproved (page 76); but admitting, for the sake of argument, that a *small* effect, which is all that can now be contended for, may thus be produced, it is altogether insignificant when contrasted with the astonishing phenomena exhibited by a voltaic circle. The experiments of A. De la Rive, in reference to this question, appear irreconcilable with the theory of Volta (An. de Ch. et de Ph. xxxviii. 225). This ingenious philosopher contends that the direction of a voltaic current is not determined by metallic contact, nor even by the nature of the metals relatively to each other, but by their chemical relation to the exciting liquid. As the result of his inquiries he states, that of two metals composing a voltaic circle, that one which is most energetically attacked will be positive with respect to the other. Thus, when tin and copper are placed in acid solutions, the former, which is most rapidly corroded, gives a positive current through the liquid to the copper, as the zinc does in the circle in fig. 1; but, if they are put into a solution of ammonia, which acts most on the copper, the direction of the current will be reversed. Copper is positive in relation to lead in strong nitric acid, which oxidizes the former most freely; whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is positive. Even two plates of copper immersed in solutions of the same acid, but of different strength, will form a voltaic circle, the plate on which chemical action is most free giving a current of positive electricity to the other: nay, it is possible to construct a compound circle solely with zinc plates and one acid solution (page 89), provided the same side of each plate be more rapidly oxidized than the other.

Conclusive evidence against the theory of Volta has very recently been obtained by Faraday. And here, to prevent repetition and frequent reference, I may at once state that the Philosophical Transactions for 1833 and 1834 contain a succession of essays on voltaic electricity from the pen of Mr. Faraday, in which numerous errors have been exposed and new views of deep interest established. It is much to affirm, but not more, I conceive, than is strictly true, that these researches, whether viewed in reference to their intrinsic value to science, or to the energy and talent displayed by the author, are equal to any of his most successful contributions. In respect to the present question, Faraday proves metallic contact not to be essential to voltaic action, by procuring that action quite characteristically without contact. A plate of zinc, *a*, fig. 11, about 8 inches long by ½ an inch wide, was cleaned and bent at a right angle: and a plate of platinum, of the same width and 3 inches long, was soldered to a platinum wire, *b s x*, the point of which, *x*, rested on a piece of bibulous paper lying upon the zinc, and moistened with a solution of iodide of potassium. On introducing the plates into a vessel, *c*, filled with dilute sulphuric and nitric acid, a positive electric current instantly ensued in the direction of the arrow, as testified by the hydrogen evolved at the plate *a*, by the decomposed iodide of potassium, and by a galvanometer. We have thus a simple circle of the same construction and action as in figure 1, except in the absence of metallic contact.

Fig. 11.



Another proof, aptly cited by Faraday, of electric excitement being independent of contact, is afforded by the spark which appears, when the wires of a pair of plates in vigorous action are brought into contact. The spark is occasioned by the passage of electricity across a thin stratum of air, and, therefore, its production proves that electro-motion really occurred while the wires were yet separated by a thin stratum of air, which permitted the electric current to pass, and anterior to their actual contact.

The arrangement of figure 11, however, though good for establishing a principle, is not adapted for ordinary practice. The moist paper at *x* is a much less perfect conductor than a metal, and thus obstructs the passage of the current; nay, it does more, for it tends to establish an opposite current. In fact, on removing the dilute acid from *c*, and putting the zinc plate, *a*, in contact with the plate of platinum, an ordinary simple circle would be formed, in which a positive current would flow from the zinc at *x* through the solution to and along the wire *x s b*. This current, in Faraday's experiment, was so feeble compared with the one excited by the acid solution, that its influence was scarcely appreciable; but if the opposed currents had been of the same force, no action would have ensued. To illustrate this still further, Faraday fixed a plate of platinum, P, figure 12, parallel and near to a plate of amalgamated zinc, Z. On placing a drop of dilute sulphuric acid at *y*, and making metallic contact between the plate at Z P, a positive electric current flowed in the direction of the arrows. If in the same plates, fig. 13, the acid be introduced at *x*, and metallic contact made at P Z, the current, passing as before from zinc through the liquid to the platinum, has a direction opposed to that of figure 2, owing to the reversed position of the acid. If, then, in the same plates, figure 14, a drop of acid be introduced at *y* and at *x*, the conditions are obviously fulfilled for producing two opposite currents of positive electricity, each fluid acting as a substitute for metallic contact in conducting the current which the other tends to generate. If these opposing currents happen to be equal, they will annihilate the effects each separately would produce; and if unequal, the stronger current, as in figure 11, will annihilate the weaker, and, though with diminished power, impress its character on the circuit.

Fig. 12.

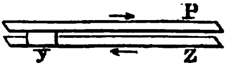


Fig. 13.

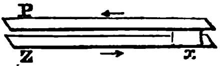
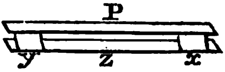


Fig. 14.



These considerations, made in reference to a simple circle, lead at once to the theory of the compound circle. For if, in figure 14, a drop of dilute acid, which acts solely on the zinc, be introduced at *y*, and a different liquid at *x*, capable of corroding platinum and not zinc, then the chemical action at *y* will cause a positive current from zinc to platinum, and that at *x* a similar current from platinum to zinc. The two currents tend to circulate in the same direction, and each promotes the progress of the other. The same state of things exists in the batteries represented by figures 8 and 9. Chemical action taking place on the zinc of each pair of plates, there is a tendency to establish an equal number of positive currents all in the same direction; and the simultaneous effort of all urges on the current with a force which it could not derive from a single pair of plates. It is now, also, apparent that all the zinc plates should have their surfaces towards one side, and those of copper towards the other: one reversed pair tends to establish a counter-current, which enfeebles the influence of the rest. On the same principle, the exciting liquid of a voltaic circle should act exclusively on one of the plates: if the copper is oxidized as fast as the zinc, opposite currents will be excited, which more or less completely counteract each other. For this reason, platinum and zinc act better than copper and zinc, especially when nitric acid is employed.

LAWS OF THE ACTION OF VOLTAIC CIRCLES.

Electricians distinguish between *quantity* and *intensity* in galvanism as in ordinary electricity. *Quantity*, in reference to a voltaic circle, signifies the quantity of electric fluid set in motion; and by *tension* or *intensity* is meant the energy or effort with which a current is impelled. In the broken circuit there is a strain to establish an electric current as a condition necessary for oxidation: there exists between the exciting fluid and the zinc a desire, as it were, for chemical action, which cannot be gratified until, by closing the circuit, a door or exit is opened for the escape and circulation of electricity. This strain or tension is great, according as the affinity between the exciting fluid and zinc is great, and the current derives a character from this tension. Nitric acid, from its great oxidizing power, causes a greater tendency to chemical action, and, therefore, to the formation of electric currents, than sulphuric acid, and this acid than a solution of salt. Currents of high tension are urged forward with greater impetuosity than feeble ones, more readily overcoming obstacles to their passage, whether derived from the small size of conducting wires, or the imperfect conduction of the liquids of the battery.

The current of a single pair of plates, though variable in intensity according as the nature and strength of the exciting liquid varies, never attains a high tension. For if the plates are far apart, the current is unable to pass at all, or at most but feebly, owing to the quantity of interposed liquid; and if close, the obstacle to be overcome in passing through a thin stratum of fluid is too small to admit of the tension being considerable. The condition which causes high intensity is an extended liquid conductor to be traversed, along the whole line of which, as in a compound circle, are ranged successive pairs of plates, each acting chemically on the exciting liquid, and urging on a current in the same direction. Under these circumstances the tension becomes very high, and the free circulation of electricity thereby occasioned enables the quantity set in motion to be also increased; but Faraday has given sufficient reasons for believing that the quantity of electricity transmitted along the wires of a closed compound circle is exactly equal in amount to that which passes through one of its cells. A compound circle does not act by directly increasing the quantity of electricity, but by giving impetus or tension to that which is excited.

The energy of a voltaic circle is usually estimated either by the deflection which it causes on a magnetic needle, or by its power of chemical decomposition. Using the former, Dr. Ritchie has obtained some interesting numerical results, of which the principal are as follows (Phil. Trans. 1832–33.)

1. The power of a single pair of plates in deflecting the magnetic needle is directly proportional to the surface of the plates which is covered with dilute acid; that is, a given deflection, produced by covering one square inch of each plate with liquid, will be doubled when two square inches are immersed.

2. A plate of zinc introduced into a rectangular cup of copper, as in figure 5, page 91, deflects the needle twice as much as when one side of the zinc and the adjacent surface of copper are protected by a coating of cement from the action of the acid solution.—The varying conditions of the experiments were calculated to affect the quantity of electricity set in motion, without changing the intensity; and, therefore, the results, proving the deflection to depend on quantity and not on tension, entirely conform to general experience.

3. The deflection produced by a pair of plates, in an acid solution of uniform strength, varies inversely as the square root of the distance between them,—a law previously established by Professor Cumming. Thus, if a plate of zinc be placed successively at one, four, and nine inches from a plate of copper, the deflecting powers will be in the ratio of 3, 2, and 1; that is, only twice as great at one inch as at four, and only three times as great at one inch as at nine inches.

4. The same law, as previously deduced by Professors Cumming and Barlow, applies to variations in the length of the wire by which the zinc and copper plate are connected. If, all other circumstances being uniform, the conducting wire varies from four feet to one foot in length, the deflecting power will vary in the ratio of 1 to 2. Dr. Ritchie informs me that with short metallic wires, the deflection varies inversely as the square root of the length of the whole circuit, that is, of the solid and liquid conductors taken together. The wire in these experiments must be single, and not coiled as in the multiplier of Schweigger: large wires should be used capable of freely conveying all the electricity which is developed.

Ritchie has also shown, agreeably to general observation, that the deflecting power of a compound circle is not increased by increasing the number of its plates. A single pair of plates with a good conducting liquid within the cell, and supplied with large conducting wires capable of carrying off the whole quantity of electricity set in motion, deflects the needle nearly or quite as much as a battery composed of several pairs of plates of the same size. This is another proof that the main influence of a number of plates is to increase the intensity and not the quantity of electricity; for the prevailing opinion that the magnetic needle takes no cognizance of intensity is fully borne out by the experiments of Faraday. The magnetic needle may be viewed as an exact measure of the quantity of electricity in motion, without any reference to its tension.

Chemical decomposition depends on quantity and intensity together, and affords a criterion of the increased tension of a compound circle due to an increase in the number of its plates. The quantity of hydrogen gas evolved by a compound circle in a given time does not vary in the simple ratio of the number of plates; that is, the volume of the gas is not doubled when the number of plates is doubled: the effect increases at a slower rate, owing to the additional obstacle to the current caused by the increased length of the circuit. Ritchie considers the ratio to be as the square root of the number of plates; so that when the number varies as 1 to 4, the gas evolved is as 1 to 2.

In discussing the preceding theoretical questions, I have gone on the assumption of electricity, as explained in the last section, being an independent principle susceptible of rapid motion from one body to another; and I have here supposed that the condition of a voltaic conducting wire is similar to that of a wire leading from the ground to the prime conductor of an electrical machine, or which connects the inner and outer surface of a charged Leyden phial, except that the voltaic current moves slowly, owing to its lower tension and the interposed imperfect conductor. Some conceive that what is called an electric current is not an actual transfer of anything, but a process of induction among the molecules of a conductor passing progressively along it. Others, denying independent materiality to electricity, may ascribe it to a wave of vibrating matter, just as the phenomena of optics are explained by the undulatory theory. But whatever theory of the nature of electricity may be adopted, it seems necessary, after the experiments of Faraday on the identity of voltaic and common electricity, that the nature of an electric and voltaic current is essentially the same.

EFFECTS OF GALVANISM.

When a zinc and copper plate are immersed in dilute acid, and the wire attached to the former is connected with a gold-leaf electrometer of sufficient delicacy, the leaves diverge with negative electricity; and on testing the wire of the copper plate in a similar manner, divergence from positive electricity is obtained. The effect is so feeble with a single pair of plates, as to be scarcely appreciable; but with a battery of many pairs it is very distinct, though never powerful. This would of course be expected, since two oppositely electrified conductors, immersed in the same liquid, would necessarily neutralize each other, unless their intensity was too feeble to find a passage through the solution. The condition of a battery which gives the greatest divergency to an electrometer is that of numerous plates; small plates an inch square being just as effectual as large ones. The free electricity on the wires is apparently an effect of the tension of the unbroken circuit, and is proportional to it, though the mode in which the effect arises is of difficult explanation. It is due, perhaps, to a disturbed electric equilibrium in the zinc plate, the chemical relation of which to the acid renders that metal positive at the expense of the attached wire; while the copper plate, induced by the contiguous zinc, becomes negative at the expense of its wire, which is thus rendered positive.

A Leyden jar may be charged from either wire of an unbroken circuit, provided the battery be in a state to supply a large quantity of electricity of high tension, as when formed of numerous four-inch plates excited by dilute acid. When the wires from such a battery are brought near each other, a spark is seen to pass between them; and on establishing the communication by means of the hands, previously moistened, a distinct shock is perceived, On sending the current through fine metallic wires or slender pieces of plumbago or compact charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the points of the charcoal, equal if not superior in intensity to that emitted during the burning of phosphorus in oxygen gas; and as this phenomenon takes place in an atmosphere void of oxygen, or even under the surface of water, it manifestly cannot be ascribed to combustion. If the communication be established by metallic leaves, the metals burn with vivid scintillations. Gold-leaf burns with a white light tinged with blue, and yields a dark brown oxide; and the light emitted by silver is exceedingly brilliant, and of an emerald-green colour. Copper emits a blueish-white light attended with red sparks, lead a beautiful purple light, and zinc a brilliant white light inclining to blue, and fringed with red. (Singer.) In burning metallic leaf, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite. The phenomena seem to arise from the current passing along these substances with difficulty; a circumstance which, as they are perfect conductors, can only happen when the quantity to be transmitted is out of proportion to the extent of surface over which it has to pass. It is, therefore, an object to excite as large a quantity of electricity in a given time as possible, and for this purpose a few large plates answer better than a great many small ones. A strong acid solution should also be used; since energetic action, though of short continuance, is more important than a moderate one of greater permanance. A mixture of ten or twelve parts of water to one of nitric acid is applicable; or, for the sake of economy, a mixture of one part of nitric to two parts of sulphuric acid may be substituted for pure nitric acid. The large battery of Mr. Children, though capable of fusing several feet of platinum wire, had an electric tension so feeble, that it did not affect the gold leaves of the electrometer, gave a shock scarcely perceptible even when the hands were moist, communicated no charge to a Leyden jar, and could not produce chemical decomposition.*

Among the effects of galvanism, produced like most of the former by a closed circuit only, and caused by electric currents, none are more surprising or so important as its chemical and magnetic effects. These will be studied successively under separate heads. For deflecting a magnetic needle, the only required condition is quantity of electricity, the amount of which is exactly measured by the degree of deflection; but for chemical decomposition quantity and tension must be combined: for the former a single pair of large plates is best fitted; for the latter a compound circle is almost essential.

Most of the effects of galvanism above described are so similar to those of the electrical machine, that it is impossible to witness and compare both series of phenomena without ascribing them to the same agent. The question of identity early occupied the attention of Wollaston, who made some very beautiful and conclusive experiments to prove that the chemical effects of galvanism may be characteristically produced by a current from the electrical machine (Phil. Trans. 1801). The subject has been examined anew by Faraday, who has subjected the effects of electricity and galvanism to a minute and critical comparison: he has obtained ample proof of the decomposing power of an electric current from an electrical machine, both by repeating the experiments of Wollaston and devising new ones of his own. He has also completed the chain of evidence by deflecting a magnetic needle with an electric current from the machine, an observation, indeed, which had been previously made by Colladon. These researches have led to a remarkable contrast between the quantity of electricity concerned in the production of voltaic and ordinary electrical phenomena. Faraday states, that the quantity of electric fluid employed in decomposing a single grain of water is equal to that of a very powerful flash of lightning; and this statement, surprising as it is, is supported by such strong evidence, that it is difficult to withhold assent to the assertion.

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* Dr. Hare has broached a very ingenious theory to account for the heat excited by galvanic action. He does not consider it probable that the heat extricated by galvanic combinations is the effect of the current of electricity passing with difficulty along conductors, in consequence of the quantity to be transmitted being out of proportion to the extent of the surfaces over which it has to pass. On the contrary, he believes that caloric, like electricity, is an *original* product of galvanic action. According to his views, the relative proportion of the two principles evolved depends upon the construction of the apparatus; the caloric being in proportion to the extent of the generating surface, and the electricity to the number of the series. In the case of batteries, in which the size and number of the plates are very considerable, both electricity and caloric are presumed by him to be generated in large quantities. When the number of the plates is very great, and their size insignificant, as in De Luc's column, electricity is the sole product; and conversely, where the size is very great and the number of the series small, caloric is abundantly produced, and the electrical effects are nearly null.—*Ed.*

Chemical Action of Galvanism.—The chemical agency of the voltaic apparatus, to which chemists are indebted for their most powerful instrument of analysis, was discovered by Messrs Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite ends of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the negative and oxygen at the positive wire. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact ratio of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas appears as usual at the negative wire; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earths, and the oxides of the common metals, were found at the negative wire; while oxygen, chlorine, and the acids, went over to the positive surface.

In performing some of these experiments, Davy observed, that if the conducting wires were plunged into separate vessels of water, made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been immersed into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated researches on the transfer of chemical substances from one vessel to another (Phil. Trans. 1807). In these experiments two agate cups, N and P, were employed, the first communicating with the negative, the second with the positive wire of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potassa or soda into N, and distilled water into P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the negative cup, leaving free acid in the other. That the acid in the first experiment, and the alkaline base in the second, actually passed along the amianthus, was obvious; for on one occasion, when nitrate of oxide of silver was substituted for the sulphate of potassa, the amianthus leading to N was coated with a film of metal. A similar transfer was effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others, and connected with each by moistened amianthus. In a short time the acid of the salt appeared in P, and the alkali in N. It was in pursuing these researches that Davy made his great discovery of the decomposition of the alkalies and earths, which till then had been regarded as elementary. (Phil. Trans. 1808.)

Such is a statement of the principal phenomena of electro-chemical decomposition according to the earlier experiments. The facts then observed were received as established truths of science, and passed current without suspicion or scrutiny till the present time. But Mr. Faraday, in his revision of this part of the science, has not only added much new matter, but proved that several points, which were considered as fundamental maxims, are erroneous. Before describing his results, however, I will define the new terms which he has had occasion to introduce.—In order to decompose a compound, it is necessary that it should be liquid, and that an electric current should pass through it, an object easily effected by dipping into the liquid the ends of the metallic wires which communicate with the voltaic circle. These extremities of the wires are commonly termed *poles*, from a notion of their exerting attractive and repulsive energies towards the elements of the decomposing liquid, just as the poles of a magnet act towards iron; and each is further distinguished by the term *positive* or *negative*, according as it affects an electrometer with positive or negative electricity. Now Faraday contends that these poles have not any attractive or repulsive energy,* and act simply as a path or door to the current: he hence calls them *electrodes*, from ηλεκτρον, and ὁδος, a way. The electrodes are the surfaces, whether of air, water, metal, or any other substance, which serve to convey an electric current into and from the liquid to be decomposed. The surfaces of this liquid which are in immediate contact with the electrodes, and where the elements make their appearance, are termed *anode* and *cathode*, from ανα, *upwards*, and ὁδος, the way in which the sun rises, and κατα, *downwards*, the way in which the sun sets. The anode is where the positive current is supposed to enter, and the cathode where it quits, the decomposing liquid, its direction, when the electrodes are placed east and west, corresponding with that of the positive current which is thought to circulate on the surface of the earth (page 117). To *electrolyze* a compound, is to decompose it by the direct action of galvanism, its name being formed from ηλεκτρον and λυω, *to unloose, or set free;* and an electrolyte is a compound which may be electrolyzed. The elements of an electrolyte are called ions, from ιον, going, neuter participle of the verb to go. *Anions* are the ions which appear at the anode, and are usually termed the electro-negative ingredients of a compound, such as oxygen, chlorine, and acids; and the electro-positive substances, hydrogen, metals, alkalies, which appear at the cathode, are *cations.* Whatever may be thought of the necessity for some of these terms, the words electrode, electrolyze, and electrolyte, are peculiarly appropriate.

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* Mr. Faraday here proves experimentally, what we threw out as a surmise, in a note contained in the last American edition of this work, as to the indispensableness of a galvanic current to the production of chemical decomposition, independently of the agency of any attractive or repulsive energy exercised by the poles, as supposed by Davy. The note referred to is in the following words:—

"If the explanation" given by Davy, "of the chemical agencies of the voltaic apparatus were well founded, then it would follow that decomposition should take place, if the same portion of water was placed in connexion, at the same time, with the positive pole of one battery and the negative pole of another. Thus the negative oxygen being attracted more strongly by the positive or zinc pole than by the positive hydrogen with which it is combined, would have its union with the latter severed, a result which would be favoured by the repulsion exercised by the positive pole on the hydrogen. Again, the positive hydrogen would be attracted by the negative pole and the oxygen be repelled. But I doubt very much whether any decomposition would take place under such circumstances; and hence I believe that a current of the galvanic fluid through compounds is essential to its decomposing powers."—*Ed.*

The principal facts determined by Mr. Faraday may be arranged under the following propositions:—

1. All compounds, contrary to what has been hitherto supposed, are not electrolytes, that is, are not directly decomposable by an electric current. But in making this assertion it is necessary to distinguish between primary and secondary decomposition. Water is an electrolyte, its hydrogen being delivered up at the negative and its oxygen at the positive electrode. A solution of hydrochloric acid is likewise an electrolyte, being resolved into chlorine and hydrogen. But nitric and sulphuric acids and ammonia are not electrolytes, though the first and last are decomposed by secondary action. Thus, on subjecting nitric acid to voltaic action, the water of the solution is electrolyzed, and its hydrogen arriving at the negative electrode decomposes the nitric acid, water being there reproduced and nitrous acid formed. So, in a solution of ammonia, the oxygen of decomposed water unites at the positive electrode with the hydrogen of the ammonia, and nitrogen gas is evolved. Very numerous secondary actions are occasioned in this way, because the disunited elements are presented in a nascent form, which is peculiarly favourable to chemical action; and in many instances the electrode itself, which is commonly metallic, is chemically attacked. By slow secondary actions of this nature, effected by very feeble currents, Becquerel has procured several crystalline compounds analogous to minerals.

2. Most of the salts which have been examined are resolvable into acid and oxide, apparently without reference to their proportions. But in compounds of two elements, the ratio of combination has an influence which has hitherto been wholly overlooked. No two elements appear capable of forming more than one electrolyte. Hydrochloric acid, and fused metallic protochlorides, such as the chlorides of lead and silver, and protochloride of tin, are readily decomposed; while bichloride of tin and other perchlorides resist decomposition. Substances which consist of a single equivalent of one element and two or more equivalents of some other element, are not electrolytes: this is the reason why sulphuric and nitric acid and ammonia do not yield primarily to voltaic action. This principle bids fair to become very important in determining which of several compounds of two elements contains single equivalents. Water, which is remarkable for its easy decomposition, may hence be inferred to be a true binary compound.

3. It has been ascertained that most of the elements are *ions,* and it is probable that all of them are so; but there are several important elements, such as nitrogen, carbon, phosphorus, boron, aluminium, and silicium, which have not yet been proved to be *ions.* This arises from the difficulty of obtaining these elements in compounds fitted for electrolytic action.

4. A single *ion,* that is, one ion not in combination with another, has no tendency to pass to either of the electrodes, and is quite indifferent to the passing current, unless it be itself a compound ion, and therefore electrolyzable. The character of true electrolytic action consists in the separation of *ions,* one passing to one electrode and another to the opposite electrode, and

appearing there at the same instant, unless the appearance of one or both be prevented by some secondary action.

5. There is no such thing as a transfer of *ions* in the sense usually understood. In order that the elements of decomposed water should appear at the opposite electrodes, there must be water between the electrodes; and for the similar separation of sulphuric acid and soda, there must be a line of particles of sulphate of soda extending from one electrode to the other. Thus, if a solution of sulphate of magnesia be covered with pure water, care being taken to avoid all admixture of particles, and the positive metallic termination or pole touch the magnesian solution only, while the negative pole is in contact with the water only, a deposite of magnesia occurs just where the pure water and the magnesian solution meet, and none reaches the negative pole. In Davy's experiment, where sulphuric acid and soda appeared to quit each other, and pass over separately into a vessel of pure water, there was certainly by capillary attraction an actual transfer of the salt before decomposition occurred.

6. In the foregoing experiment a surface of water acts as the negative electrode, clearly showing the contact of a metallic conductor with the decomposing liquid not to be essential. Faraday has proved that even air may serve as an electrode. A current from the prime conductor of an electrical machine was made to pass from a needle's point through air to a pointed piece of litmus paper moistened with sulphate of soda, and then to issue from a similarly moistened point of turmeric paper. True electrolytic action took place, the litmus becoming red and the turmeric paper brown, though both extremities of the decomposing solution communicated solely with a stratum of air.

7. Electro-chemical decomposition cannot occur unless an electric current is actually transmitted through it; or, in other terms, an electrolyte is always a conductor of electricity. Water, which conducts an electric current, ceases to do so when it passes into ice, and then also resists decomposition—an observation equally true of all electrolytes in becoming solid. Moreover, liquids which resist electro-chemical decomposition do not permit the current of a voltaic circle to pass. The alliance between conduction and decomposition is so constant, that the latter may be regarded as a means by which voltaic currents are transmitted through liquid compounds. Agreeably to this notion, solidity may interfere with conduction by chaining down the elements of a compound, and thereby preventing their transfer to the electrodes. Improving the conduction of a liquid, as by adding sulphuric acid to pure water, increases the decomposing power of a voltaic circle, the exciting fluid within the apparatus remaining the same; and Faraday has proved that the quantity of a compound decomposed is exactly proportional to the quantity of electricity which passes, however much other circumstances, such as the size of electrodes and conducting wires, number and size of plates, and nature of exciting fluid, may vary. Changes in these conditions do, indeed, influence the quantity of electricity transmitted; but then the degree of chemical decomposition varies in the same proportion. The foregoing facts at first led to the opinion that the current of a voltaic circle cannot pass through liquids, except those of a metallic nature, unless decomposition ensues at the same time; but Faraday has noticed that when the intensity is too feeble to effect decomposition, a small quantity of electricity may be transmitted, sufficient to be discovered by a galvanometer. This does not, however, essentially interfere with the law just announced.

8. Chemical compounds differ in the electrical force required for decomposition. A current of very feeble tension suffices to decompose iodide of potassium, while a much higher intensity is required for disuniting the elements of water. The order of easy decomposition in the annexed substances is as follows:—Solution of iodide of potassium; fused chloride of silver; fused protochloride of tin; fused chloride of lead; fused iodide of lead; solu-

tion of hydrochloric acid; and water acidulated with sulphuric acid. By extending tables of this kind, a ready method will be known for comparing the tension of voltaic circles.

9. The conduction of the electric currents within the cells of a voltaic circle depends on chemical decomposition equally with that between platinum electrodes. No substance not an electrolyte can serve to excite a voltaic apparatus; and for the passage of electricity from plate to plate through the intervening solution, the separation of substances previously combined in the required ratio is essential. Neither free oxygen nor a solution of chlorine can excite a current, though they attack the zinc; and in a voltaic circle excited by dilute sulphuric acid, the electricity set in motion is due to decomposed water and oxidized zinc, and not at all to the union of the oxide of zinc with sulphuric acid. The platinum electrodes and intervening liquid may be viewed as one of the cells of the circle, except that the plates act merely as conductors, without any oxidation, the current passing in virtue of the decomposed solution. Thus, in figure 9, page 92, the zinc and copper plate of either of the glasses may be replaced by two plates of platinum; or several pairs of such plates may be introduced in any part of a compound circle, in which case the intervening spaces are cells of decomposition only. But such plates diminish very much the power of a battery. In the zinc and copper cells, the current is urged on by the appetency of the zinc and oxygen to unite; whereas, in passing between the electrodes, the electricity has to surmount the mutual attraction of oxygen and hydrogen, or some similar force, without the assistance of any opposing affinity. In overcoming this obstacle, the electric current is enfeebled; and if its tension is insufficient for decomposing the interposed liquid, it is almost completely arrested. Hence, in experiments on decomposition, the course of the electricity should be facilitated by employing large electrodes and wires, and placing them at a short distance from each other in a good conducting solution.

The principles above established show the importance of exciting all the cells of a voltaic circle with a liquid of the same strength. The electricity circulating in a voltaic apparatus with the conducting wires in contact, is equal to that which the feeblest cell is able to transmit, any chemical action in other cells more than sufficient for exciting that quantity being wasted; and in a circle with several decomposing cells, the current which traverses the cell of lowest conducting power determines the quantity circulating through the whole apparatus.

10. In a voltaic circle in which no zinc is oxidized but what contributes to excite an electric current, the quantity of zinc dissolved in a given time from each plate is in a constant ratio, not only to the hydrogen gas evolved from the corresponding copper plate (page 94), but to the hydrogen set free at the negative electrode. The ratio is such, that 32.3 parts of zinc are dissolved during the evolution of 1 part of hydrogen gas; and the conclusion which Mr. Faraday has drawn from this and numerous similar experiments is, that the quantity of electricity set in motion by the oxidation of 32.3 grains of zinc exactly suffices for resolving 9 grains of water into its elements. If the same current, by means of 4 pairs of electrodes, be made to decompose water, chloride of silver, chloride of lead, and chloride of tin, all in the liquid state, the quantities of hydrogen, silver, lead, and tin eliminated at the 4 negative electrodes will be in the ratio of 1, 108, 103.6, and 57.9; while, a tone positive electrode, oxygen, and at the three others chlorine, in the ratio of 8 to 35.4, are separated. Similar facts were ascertained of many other compounds. It thus distinctly appears—and it is a new and important discovery—that electro-chemical decomposition is perfectly definite, a given quantity of electricity evolving the ingredients of compound bodies in well defined and invariable proportions, to which Faraday has given the name of *electro-chemical equivalents*. The reader will at once see that these numbers are identical with the chemical equivalents (see table part ii, sect. II). Another connexion, then, closer than any before traced, is established between electricity and chemical

attraction, showing a mutual dependence and similarity of effect between two agencies, such as almost forces a belief in their identity.

The definite nature of electro-chemical action suggests a ready mode of estimating the quantity of electricity circulating in a voltaic apparatus. It is only necessary to collect the gas evolved from acidulated water, in order to obtain a measure of the quantity of electricity which has passed during a given interval: a tube divided into equal measures will thus serve to express degrees of electricity, just as the expansion of a liquid in a thermometer indicates degrees of temperature. The instrument, as constructed for this object, is called by Faraday a *volta-electrometer*. Various forms of it have been described by him, according as it wished to collect oxygen or hydrogen separately, or both together. One of the most convenient forms, which collects the gases together, is exhibited by figure 15. It consists of a glass tube closed at bottom, where it fits into a support of wood A; the wires *p n* serve to connect it with a closed circle; and *a b* are large platinum electrodes, placed close together, but prevented from contact by interposed beads of glass. The tube when prepared for use, is filled up to the bend with dilute sulphuric acid of sp. gr. 1.336; and the gas evolved, escaping from the open extremity *c*, is collected in a tube and measured.

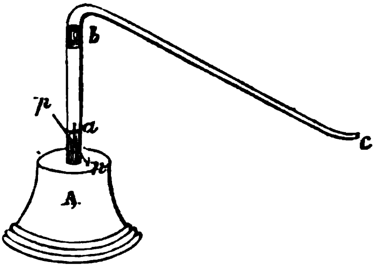
Fig. 15.

Theory of Electro-chemical Decomposition.—The most celebrated attempt to explain the phenomena of galvanism was made by Davy in his essay on *Some Chemical Agencies of Electricity* (Phil. Trans. 1807), by means of an hypothesis which has received the appellation of the *electro-chemical theory*. The views of Davy, which in some form or other have been adopted by most persons who have speculated on this subject, are founded on the assumption, now rendered so much more plausible than in his day, that electrical and chemical attractions are owing to one and the same agent. He considered chemical substances to be endowed with *natural electric energies;* meaning thereby, that a certain electric condition, either positive or negative, is natural to the atoms or combining molecules of bodies; that chemical union is the result of electrical attraction taking place between oppositely excited atoms, just as masses of matter when oppositely excited are mutually attracted; and that ordinary chemical decomposition arises from two combined atoms being drawn asunder by the electric energies of other atoms more potent than those by which they were united. Electro-chemical decomposition was at once explained by Davy on the same principles. He regarded the metallic terminations or *poles* of a voltaic circle (page 102) as two centres of electrical power, each acting repulsively to particles in the same electric state as itself, and by attraction on those which were oppositely excited. The necessary result was, that if the electric energy of the battery exceeded that by which the elements of any compound subject to its action were held together, decomposition followed, and each element was transferred bodily to the pole by which it was attracted, passing through solutions not containing the original compound, and refusing to unite with substances with which under other circumstances it would have combined. Substances which appeared at the positive pole, such as oxygen, chlorine, and acids, were termed *electro-negative* substances; and those *electro-positive* bodies, which were separated at the negative pole.

The views of Davy, both in his original essay and his subsequent explanations (Phil. Trans. 1826), were so generally and obscurely expressed, that chemists have never fully agreed, as to some points of the doctrine, about his real meaning. If he meant that a particle of free oxygen or free chlorine is in a negatively excited state; then his opinion is contrary to the fact, that neither of those gases affect an electrometer with negative or any kind of electricity, any more than hydrogen gas or potassium alone exhibit any evidence of positive excitement. If sulphur unites with oxygen because it has a positive electric energy, why should it unite with potassium, which confessedly is far more positive than itself? The only mode in which such facts as these seem reconcilable with the electro-chemical theory, is to suppose all bodies in their uncombined state to be electrically indifferent, but that they have a natural appetency to assume one state in preference to another. Electro-negative bodies are such as assume negative excitement under a certain approximation to others which at the same time become positively excited, chemical union being the consequence. On this supposition, it is intelligible that sulphur may be positive in relation to oxygen, and negative to potassium, just as black silk is positively electrified by friction with sealing-wax, and negatively by white silk. It is obvious, from the following table constructed by Berzelius, that this chemist takes the same view of the electric energies of bodies as that just given. He has given it as approximative only, and not as rigidly representing the exact electrical relations of the elements. Nitrogen and hydrogen scarcely occupy their true position in the series, the former being electro-negative in a lower degree than chlorine and fluorine, while hydrogen, I think, should be in a prominent station among the electro-positive elements. All the bodies enumerated in the first column are negative to those of the second. In the first column each substance is negative to those below it; and in the second, each element is positive with reference to those which occupy a lower place in the series.

1.

Negative Electrics.

Oxygen.
Sulphur.
Nitrogen.
Chlorine.
Iodine.
Fluorine.
Phosphorus.
Selenium.
Arsenic.
Chromium.
Molybdenum.
Tungsten.
Boron.
Carbon.
Antimony.
Tellurium.
Columbium.
Titanium.
Silicium.
Osmium.
Hydrogen.

2.

Positive Electrics.

Potassium.
Sodium.
Lithium.
Barium.
Strontium.
Calcium.
Magnesium.
Glucinium.
Yttrium.
Aluminium.
Zirconium.
Manganese.
Zinc.
Cadmium.
Iron.
Nickel.
Cobalt.
Cerium.
Lead.
Tin.
Bismuth.
Uranium.
Copper.
Silver.
Mercury.
Palladium.
Platinum.
Rhodium.
Iridium.
Gold.[*]

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[*] The statements made in the text are, perhaps, not expressed with suf-

It requires but little reflection on the facts described in this section, to perceive that they are inconsistent with the electro-chemical theory as understood by Davy. It gives not the shadow of a reason for a voltaic battery which can decompose the protochloride or protiodide of a metal, being powerless with the perchloride and periodide of the same metal. The fact itself was not contemplated by Davy, and his theory was designed to show why all such compounds should be decomposed. Moreover, there is no proof that the poles of a battery do exert attractive or repulsive forces. There is no need of a metallic conductor in contact with the decomposing body (page 104); nor do the elements reach the poles at all, unless they happen to be in contact with the substance under decomposition (page 104). When hydrogen reaches the negative electrode, it is freely disengaged as gas, the electrode evincing no tendency whatever to retain it: the combination of the elements of a decomposed body with the matter of the electrodes, does not prove attraction, but may, and I presume does, arise from the substances being presented in a state favourable for chemical union (page 103). But while Davy's theory fails, there is no other which can render a reason for all the phenomena. Faraday has done much by showing the fallacy of the former theory, and by stating the facts of the case as they are. He contends that, between the electrodes and acting in right lines, there is an axis of power which urges the electro-negative element of an electrolyte in the direction the positive current moves, and gives an opposite impulse to the electro-positive element. He adopts the opinion of Grotthuss, that the decomposing influence is not exerted on any single particle of the electrolyte, but that rows of particles lying between the electrodes are equally subject to its action. When a particle of oxygen is evolved at the positive electrode, the hydrogen with which it had been combined is not transferred at once to the opposite electrode, but unites with the oxygen of a contiguous particle of water, on the side towards which the positive current is moving; the second particle of hydrogen decomposes a portion of water still nearer to the negative electrode; and the same process of decomposition and reproduction of water continues until it reaches the water in immediate contact with the negative electrode, the hydrogen of which is disengaged. This operation, described as commencing at one electrode, takes place simultaneously at both: a row of particles of oxygen suddenly lose their affinity for the hydrogen situated on the side next the negative electrode, in favour of those respectively adjacent to each on the other side; while the affinity of a similar row of particles of hydrogen is diminished for the oxygen on the side of the positive electrode, and is increased for those on their opposite side. Hence, as

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ficient clearness for the comprehension of the student. The doctrine laid down by Dr. Turner is, that substances, considered singly, are neither positive nor negative; or in other words, that they are in a neuter state like the earth. Nevertheless, they are capable of exciting each other by being first brought in contact, and then separated. If two substances touch each other, and are then separated, one will become positive and the other negative; but the result is not conclusive as to the electric energy of either, because the electric state of each may possibly be reversed by contact with some other substance. These positions are rigidly exact with respect to all the simple substances, except oxygen and potassium; for, as the former yields electricity to all other substances, it must always be negative, and as the latter takes electricity from all other substances, it must be invariably positive. Thus it is plain that the electric energy of none of the simple bodies is absolute, except that of oxygen and potassium; while the electric energy of the remaining simple bodies is relative, and is either positive or negative, according to circumstances. It is for these reasons that I have thought that the arrangement of bodies into negative and positive electrics, as Dr. Turner has done, after Berzelius, is objectionable, as leading the student into the error of supposing that each group was in its own nature either negative or positive.—*Ed.*

is the fact, for the elimination of the elements of an electrolyte at the electrode, it is essential that the electrolyte itself should occupy the space between the electrodes, and be in contact with them. The theory, however, is at present incomplete: it affords no reason for the disturbed order of affinities in the elements of an electrolyte; nor is it apparent how the chemical changes between the electrodes are so essential as they seem to be (page 104) to the passage of the currents.

Magnetic Effects of Galvanism.—The power of lightning in destroying and reversing the poles of a magnet, and in communicating magnetic properties to pieces of iron which did not previously possess them, was noticed at an early period of the science of electricity, and led to the supposition that similar effects may be produced by the common electrical and voltaic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity and galvanism; but no results of importance were obtained till the winter of 1819, when Professor Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science. (Annals of Philosophy, xvi. 273.)

The fact observed by Professor Oersted was, that the metallic wire of a closed voltaic circle, and the same is true of charcoal, saline fluids, and any conducting medium which forms part of a closed circle, causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the relative position of the needle and the wire. On placing the wire above the magnet and parallel to it, the pole next the negative end of the battery always moves westward; and when the wire is placed under the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side. Ampère has suggested a useful aid for recollecting the direction of these movements. Let the observer regard himself as the conductor, and suppose a positive electric current to pass from his head towards his feet, in a direction parallel to a magnet; then its north pole in front of him will move to his right side, and its south pole to his left. The plane in which the magnet moves is always parallel to the plane in which the observer supposes himself to be placed. If the plane of his chest is horizontal, the plane of the magnet's motion will be horizontal; but if he lie on either side of the horizontally suspended magnet, his face being towards it, the plane of his chest will be vertical, and the magnet will tend to move in a vertical plane.

The extent of the declination occasioned by a voltaic circle depends upon its power, and the distance of the connecting wire from the needle. If the apparatus be powerful, and the distance small, the declination will amount to an angle of 45°. But this deviation does not give an exact idea of the real effect which may be produced by galvanism; for the motion of the magnetic needle is counteracted by the magnetism of the earth. When the influence of this power is destroyed by means of another magnet, the needle will place itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

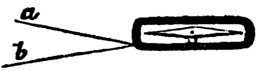
The communicating wire is also capable of attracting and repelling the poles of a magnet. This is easily demonstrated by permitting a horizontally suspended magnet to assume the direction of north and south, and placing near it the conducting wire of a closed circle, held vertically and at right angles to the needle, the positive current being supposed to flow from below upwards. When the wire is exactly intermediate between the magnetic poles, no effect is observed; on moving the wire nearly midway towards the north pole, that is, to the pole which points to the north, the needle will be attracted; and repulsion will ensue when the wire is moved close to the north pole itself. Similar effects occur on advancing the wire towards the south pole. Such are the phenomena if the positive current ascend on the west side of the needle; but they are reversed when the wire is placed vertically on the east side. Attractions and repulsions likewise take place in a dipping needle, when the current flows horizontally across it.

The discovery of Oersted was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful of those who early distinguished themselves were Ampère, Biot, and Arago, of Paris, and Davy and Faraday in this country. A host of other able men have since added their contributions; and their joint labours have established an altogether new science, *Electro-Dynamics*, which has already become one of the most important branches of physical knowledge, and still offers a rich harvest of discovery to its cultivators. Those who wish to enter deeply into the study of this subject should consult the *Recueil d'Observations Electro-Dynamiques* by Ampère, Professor Cumming's Manual of Electro-Dynamics, Mr. Murphy's Treatise on Electricity, and the second edition of Mr. Barlow's Essay on Magnetic Attractions. A less mathematical, and, therefore, more generally intelligible treatise has been drawn up with great ability by Dr. Roget, and published as part of the Library of Useful Knowledge; and a Popular Sketch of Electro-Magnetism has been given by Mr. Watkins of Charing-cross. To these works I refer as supplying that detail of the facts and theories of electro-dynamics, which, as belonging more to the province of physics than chemistry, is unsuited to the design of this volume. My object is merely to give an outline of the discoveries in electro-dynamics, and to convey an idea of the nature and present state of the Science.

The phenomena of electro-dynamics are solely produced by electricity in motion. Accumulated electricity giving rise to tension, which acts so essential a part in experiments with the electrical machine, has no influence whatever on a magnetic needle. The passage of electricity through solid or liquid conductors is essential; and it is remarkable that the more freely the current is transmitted, that is, the more perfect the conducting substance, the more energetic is its deflecting power. In fact, a magnetic needle is a *Galvanoscope*, by which means the existence and direction of an electric current may be detected. It was early employed with this intention by Ampère, who found that a voltaic apparatus itself acts on a magnetic needle placed upon or near it in the same manner as the wire which unites its two extremities; but as the deflection took place only when the opposite ends of the battery were in communication, and ceased entirely when the circuit was broken, he inferred that electricity passes uninterruptedly through the battery itself when the circuit is closed, and not at all in the interrupted circuit.

But a magnetic needle will not only indicate the existence and direction of an electric current: it may even serve, by the degree of deflection, as an exact measure of its force. When used for this purpose, under the name of *Galvanometer*, some peculiar arrangements are required in order to ensure the requisite delicacy and precision. Experiment proves that a magnet is equally affected by every point of a conductor along which an electric current is passing, so that a wire transmitting the same current will act with more or less energy, according as the number of its parts contiguous to the needle is made to vary. On this principle is constructed the *Galvanometer* or *Multiplier* of Schweigger. A copper wire is bent into a rectangular form consisting of several coils, and in the centre of the rectangle is placed a delicately suspended needle, as shown in figure 16. Each coil adds its influence to that of the others; and as the current, in its progress along the wire, passes repeatedly above and below the needle in opposite directions, their joint action is the same. In order to prevent the electricity from passing laterally from one coil to another in contact with it, the wire should be covered with silk. The ends of the wire, *a* and *b*, are left free for the purpose of communication with the opposite ends of the voltaic circle. When a single needle is employed, as shown in the figure, its movements are influenced partly by the earth's magnetism, and partly by the electric current. The indications are much more delicate when

Fig. 16.

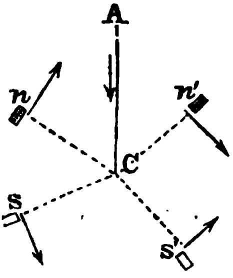


the needle is rendered *astatic*, that is, when its directive property is destroyed by the proximity of another needle of equal magnetic intensity, fixed parallel to it, and in a reversed position, each needle having its north pole adjacent to the south pole of the other: in this state the needles, neutralizing each other, are unaffected by the magnetism of the earth, while they are still subject to the influence of galvanism. If, as in the last figure, the lower needle lie within the rectangle, and the upper needle just above it, the electric current flowing between will act on both in the same manner. For researches of delicacy the needle should be suspended by a slender long thread of glass, and the deflecting force measured, not by the length of the arc traversed by the needle, but by the torsion required to keep the needle at a constant distance from the wire, as in the torsion electrometer of Couloumb (page 81.) A very valuable instrument on this principle has been described by my colleague Dr. Ritchie (Royal Inst. Journal, N. S. i. 31.)

The mutual influence of a magnetic pole and a conducting wire changes with the distance between them. Experiment shows that the action of a magnetic pole and a continuous conductor, every point of which exerts a separate energy on the pole, varies inversely as the distance. This result justifies the opinion that the force of a magnetic pole on a *single* point of a conductor varies as the square of the distance, the same law which regulates the distribution of heat and light, as well as the effects due to electricity.

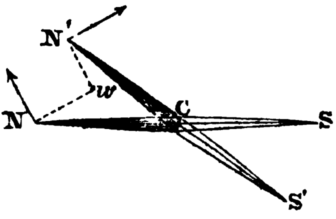
From some of the experiments of Oersted above mentioned, it was at first believed that a force, one while attractive and at another repulsive, acted in straight lines between the magnet and conducting wire; but on examination all the phenomena are found referable to a force acting tangentially upon the poles of a magnet, and in a plane perpendicular to the direction of the current. Place, for instance, a blank card flat on the table, and fix a wire A C upright in its centre. If, then, a positive electric current pass up or down the wire, a magnetic pole resting on the card, will be inclined to move in the plane of the card, and, therefore, at right angles, to the current, and to describe a circle round C as its centre. If a north pole be at *n* and *n′*, and a south pole at *s* and *s′*, and a positive current descend as shown by the arrow in figure 17, let fall from each pole a dotted line perpendicular to the wire at C, and each dotted line will be the radius of the circle in which the corresponding pole will rotate. All the north poles will move in the line of the tangent directed to the right of the radius, and will have the same course as the hands of a watch when it is placed on a table with the dial plate upwards; and the south poles will rotate in the opposite direction. Should the electric current be ascending, the rotation of each pole will be reversed. If the current move horizontally, the plane of rotation will be vertical; and if figure 17 be moved into this position, the positive current still flowing from A to C, the arrows on the card will still indicate the course of rotation.

Fig. 17.



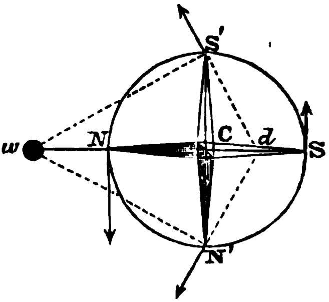
The movements first observed by Oersted (page 109) are referable to this principle. When a magnetic needle, movable round the middle of its axis, is acted on by a parallel current, its poles receive an equal but contrary impulse, and the needle consequently comes to rest across the direction of the current. If a vertical positive current be placed, as shown in figure 18, at *w*, on the right side of a horizontal needle N S, movable round C, the pole N will move towards it; but if the current continue at *w* while the magnet occupies the position of N′ S′,

Fig. 18.



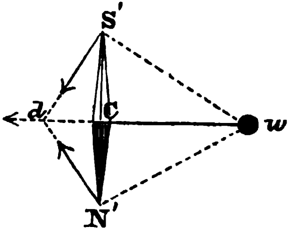
the pole N′ will recede from the current: thus there is the appearance of repulsion in one case and of attraction in the other.

Fig. 19.



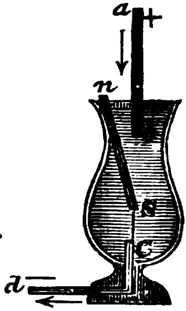
If a similar current were without the circle in which a horizontal magnet moves, as at *w* in figure 19, then the magnet, stationary at N S, would at first have its poles impelled in opposite directions; but when it reaches the position N′ S′, the force at each pole acts on the same side of the magnet's axis. The poles also, being equidistant from *w*, and having the same inclination, will be influenced by equal forces acting at the same mechanical advantage. They will, therefore, by the laws of equilibrium, have a resultant which will pass directly through the centre of motion. This resultant, represented as applied at *d*, will tend to draw the wire *w* and the middle of the magnet C directly towards each other. If the conducting wire *w* were on the right instead of the left side of the magnet, as in figure 20; then the resultant, passing as before through the centre of motion, but in an opposite direction, tends to draw the magnet and wire directly from each other, and to give the appearance of repulsion.

Fig. 20.



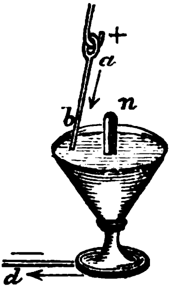
The same principle accounts for the rotation of a magnetic pole round a current, discovered by Faraday. Into the centre of the bottom of a cup, as in the vertical section, figure 21, a copper wire c *d* was inserted, a cylindrical magnet *n* s was attached by a thread to the copper wire c, and the cup was nearly filled with mercury, so that the pole *n* only of the magnet projected. A conductor *a b* was then fixed in the mercury perpendicularly over the wire c. On connecting the conducting wires with the opposite ends of a battery, a current was transmitted from one wire through the mercury to the other. If the positive current descend, the north pole of the magnet, if uppermost, will rotate round the wire *a b*, passing from east through the south to west like the movements in the hands of a watch; and if the current ascend, the line of rotation will be reversed. Under similar circumstances the south pole would in each case rotate in the opposite direction.

Fig. 21.



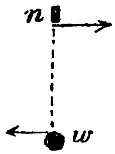
If a magnetic pole rotate round a conductor, a conductor will be equally disposed to rotate round a magnetic pole, just as a magnet moves towards iron or iron towards a magnet, according as one or other is free to move. Accordingly, on fixing a magnet vertically in the middle of a cup of mercury, fig. 22, and transmitting a current by the moveable conductor *a b* through the mercury, and along a second conductor *d*, fixed as before in the bottom of the cup, Faraday found that the free extremity *b* of the wire moved round the pole of the magnet in a direction similar to the last.

Fig. 22.



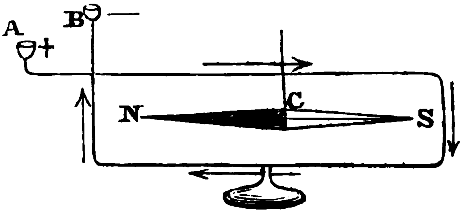
It is obvious that the direction of rotation imparted by a fixed current to the moveable pole, will be identical with that which the same pole tends to impart to the same current. Thus let *w* in figure 23 represent the section of a wire along which a positive electric current is descending, and *n* the north pole of a magnet. If *w* impel *n* towards the right side, *n* will give an impulse to *w* in the opposite direction, as indicated by the arrows. Each is disposed to describe a circle round the other as a centre, moving in the same direction as the hands of a watch with its dial upwards; and if *w* and *n* were equally free to move, they would act as a couple in statics, and tend to rotate round the middle of the dotted line which joins them.

Fig. 23.



The advantage of the rectangular form in the construction of a galvanometer (page 110) will now be intelligible. A magnetic needle N S, pointing north and south, and suspended by the point C horizontally within the rectangle, figure 24, will be influenced in the same manner by each of its sides. If the positive electric current flow from A horizontally above the needle from north to south, and then successively along the other three sides up to B, the separate influence of each side, agreeably to the principle above illustrated, will impel the north pole eastward, and the south to the west. The little cups A B are designed to contain mercury, and afford a ready means of connecting the rectangle with the opposite sides of a galvanic combination.

Fig. 24.



If the rectangle, in the last combination, have the property of impelling the north pole of a magnet to its right side, the north pole, when placed on that side, will give an opposite impulse to the rectangle. This may be shown by an elegant apparatus of De la Rive, which consists of a circular copper wire, the extremities of which are passed through a cork, and soldered to a plate of zinc and copper. On placing the arrangement in a vessel of acidulated water, a positive electric current passes from the copper plate round the circle to the zinc, as shown in figure 25; and as the cork renders the apparatus buoyant, a very slight force will throw it into motion. It will exhibit various phenomena of attraction and repulsion, all explicable on the principle already explained, according to the relative position of the magnetic pole which is presented. The apparatus will be more powerful if the conducting wire, covered with silk, to prevent lateral communication, be formed into several circles of the same diameter, on the principle of the multiplier.

Fig. 25.

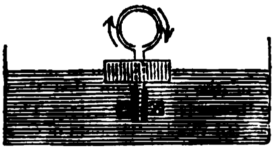
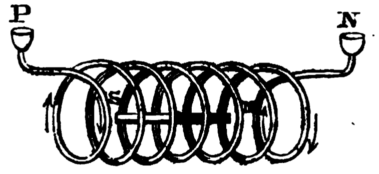


Fig. 26.

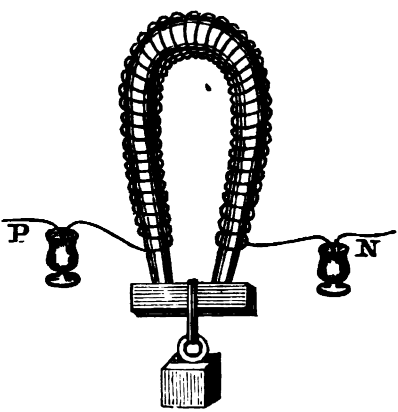


A current of voltaic electricity not only determines the position of a magnet, but renders steel permanently magnetic. This was observed nearly at the same time by Arago and Davy, who found that when needles are placed at right angles to the conducting wire, permanent magnetism is communicated;

and Davy also succeeded in producing this effect even with a shock of electricity from a Leyden phial. Arago, at the suggestion of Ampère, made a voltaic conductor into the form of a helix, into the axis of which he placed a needle, as in figure 26. As in this arrangement the current nearly in every part of its course is at right angles to the needle, and as each coil adds its effect to that of the others, the united action of the helix is extremely powerful. The needle was thus fully magnetized in an instant.

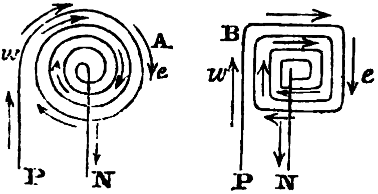
Though soft iron does not retain magnetism, its magnetic properties while under the influence of an electric current are very surprising. A piece of soft iron about a foot long and an inch in diameter is bent into the form of a horse-shoe, a copper wire is twisted round the bar at right angles to its axis, and an armature of soft iron, to which a weight may be attached, is fitted to its extremities, as in figure 27. On connecting the ends of the wire with a simple voltaic circle, even of small size, the soft iron instantly becomes a powerful magnet, and will support a weight of 50, 60, or even 70 pounds. Increasing the number of coils gives a great increase of power; but as the length of wire required for that purpose diminishes the influence of the current (page 97), the following arrangement has been successfully adopted. The total length of copper wire intended to be used is cut into several portions, each of which, covered with silk or cotton thread to prevent lateral communication, is coiled separately on the iron. The ends of all the wires are then collected into two separate parcels, and are made to communicate with the same voltaic battery, taking care that the positive current shall pass along each wire in the same direction. The current is thus divided into a number of branches, and has only a short passage from one end of the battery to the other, though it gives energy to a multitude of coils. A combination of this kind, connected with a battery of five feet square, supported 2063 pounds, or nearly a ton weight.

Fig. 27.



In witnessing the influence of voltaic conductors over the directive property of magnets, and in inducing magnetism, it is difficult to divest one's self of the conviction that these conductors, while transmitting a current, are themselves magnetic. This belief was early entertained by those who repeated the experiments of Oersted, and experimental evidence of its truth was speedily adduced. Arago and Davy found that a copper wire connecting the end of a voltaic combination attracted iron filings, but that they instantly fell off as soon as the circuit was broken; and a conductor, when its movements were not impeded by friction or gravity, was proved by Ampère to be obedient, like an ordinary magnet, to the magnetic agency of the earth. Though these properties may be exhibited by a single wire, the action is more conspicuous when, on the principle [illegible] multiplier, the con[illegible]ted into a spiral, [illegible] 28, or into a rect-

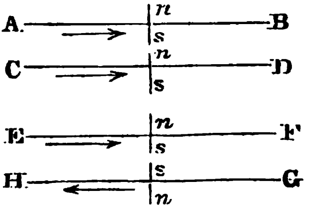
Fig. 28.



angular form as represented by B in the same figure. When the arrangement is connected with a floating galvanic combination as in figure 25, or is very delicately suspended, the plane of the spiral places itself east and west, the positive current ascending on the west side and descending on the east: the positive current, in fact, takes the same course as the hands of a watch, when it is held on edge with the plane of the dial lying east and west, facing the south. That side of the spiral which is towards the north, consistently with an experiment already mentioned (page 113), acts as the north pole; and the south side of the spiral has an opposite polarity. Each side is powerfully attractive to iron filings. Another convenient form of the conductor is the helix, figure 26. Each coil of the helix is a separate magnet, and tends to place itself in the same position as the spiral or rectangle; but the multiplied effect of all the coils causes north and south polarity to be accumulated at the opposite ends of the helix, and, therefore, to be separated, not by the mere thickness of the wire, but by the whole length of the helix.

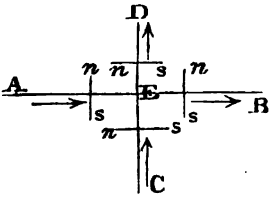
Since, therefore, the conductors just described may be regarded as magnets, such magnetized conductors ought mutually to repel or attract each other, when poles of the same or a different nature are adjacent; and as the action of a whole spiral or rectangle is merely the accumulated effect of its individual parts, it is fair to presume that each small portion of a conductor has its opposite sides in a state of opposite polarity, and that two such contiguous portions should attract or repel each other on the same principle as the spirals of which they constitute a part. Nay, even different parts of the same conductor ought to be mutually attractive or repulsive. These inferences from the facts already detailed, were fully demonstrated by Ampère soon after the discovery of Oersted. He proved that two voltaic conductors, or two portions of the same conductor, attract each other when the currents have the same direction, and are mutually repulsive when they are traversed by opposite currents; which is exactly what would be anticipated from the magnetic influence of conductors. Thus, in the two parallel positive currents, AB and CD, figure 29, which flow in the same direction, the contiguous sides are affected with an opposite polarity, one being south and the other north; whereas in the two contrary currents, EF and GH, the adjacent sides have the same polarity, and therefore repel each other.

Fig. 29.



Similarly when two currents cross each other, as AB and CD, figure 30, it is obvious that at two of the four corners, AD and CB, similar poles are contiguous; while at the other corners different poles concur. Hence the wires tend to revolve round E, and place themselves parallel to the currents so that both may flow in the same direction.

Fig. 30.



If a moveable conductor CD be wholly on one side of AB, as in figure 31, repulsion will ensue on one side and attraction on the other. The direction in which these forces act is indicated by the dotted arrows, *e b* and *e g*; and they give a resultant *e r*, which tends to draw CD to the right side.

Fig. 31.

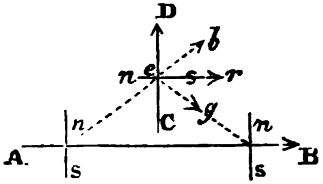


Fig. 32.

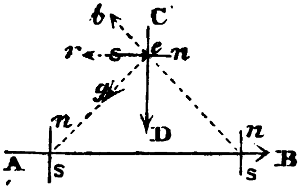
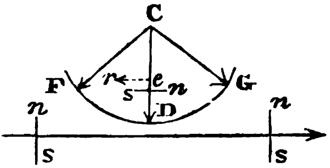


Figure 32 shows the effect of reversing the current in C D, which will consequently be drawn by a force at right angles to itself to the left side.

Fig. 33.

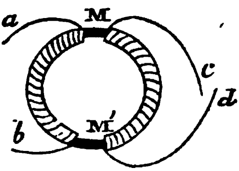


If in the last case the conductor C D were moveable round C as a centre, then the resultant *e r* would draw D towards F, figure 33; but if the current in either conductor were reversed, C D would tend to rotate towards G.

These are a few examples of the numerous facts experimentally proved by Ampère concerning the action of voltaic conductors on each other. It is to this branch of the subject the term of *Electro-Dynamics*, or the science of electricity in motion, is sometimes restricted, while the mutual action of conductors and magnets is called *Electro-Magnetism;* but these two branches are so entirely parts of the same science, that I have included both under Ampère's term of Electro-Dynamics. Any one who has studied the few preceding pages with moderate care, cannot fail to trace a close analogy between a helix traversed by an electric current and a magnet. The former is affected by other voltaic conductors, by the poles of a magnet, and by the magnetism of the earth, in the same manner as the latter. It was this similarity, or rather identity, of action which led Ampère to his theory of magnetism. He supposes that the polarity of every magnet is solely owing to the circulation, within its substance and at its surface, of electric currents, which continually pass around all its particles in planes perpendicular to its axis. On placing a magnet in its natural position of north and south, the direction of its currents is exactly the same as in the conductors of figure 28, descending on the east side, passing under the magnet from east to west, and ascending on the side next the west. In like manner are currents supposed to circulate within the earth, especially near its surface, passing from east to west in planes parallel to the magnetic equator. These terrestrial currents cause all bodies, which are freely suspended, and are possessed of electric currents, to place themselves in such a position that the current on their under side should flow in parallelism, and in the same direction, with that in the earth immediately beneath. That the existence of such currents will account for the directive property of the earth, follows from the mutual action of conductors; and Mr. Barlow, to render the analogy still more complete, constructed a hollow sphere of wood, in which electric currents were made to circulate in the same direction as they are thought to do in the earth; and by placing an astatic needle on different parts of its surface, he found that all the phenomena of terrestrial magnetism might be imitated. Observation has even supplied a cause for the existence of currents in the earth, moving in the direction which theory requires. The diurnal rotation of our planet on its axis exposes its surface to be heated in a direction passing from east to west; and the discoveries which have been made in thermo-electricity (page 75) sufficiently prove the probability of electric currents being established in the conducting matter of the earth by the successive heating of its parts. In short, the theory of Ampère connects the facts of electro-dynamics with the phenomena of terrestrial magnetism, and affords a splendid instance of the application of mathematical analysis to physical research.

Volta-electric Induction.—The development of electricity by the vicinity of an excited body, already described under the name of induced electricity (page 78), led Mr. Faraday to inquire whether electricity in motion, as well as that of tension and at rest, may not be excited by induction. Though baffled in his early attempts, he at last succeeded in laying open a new branch of electro-dynamics, which vies in interest and importance with the fundamental discovery of Oersted (Phil. Trans. 1831). A copper wire 203 feet long was passed in form of a helix round a large block of wood, and an equal length of a similar wire was wound on the same block and in the same direction, so that the coils of each helix should be interposed, but without contact, between the coils of the other. The ends of one of the helices were connected with a galvanometer, and the other with a strong galvanic battery, with the view of ascertaining whether the passage of an electric current through one helix would induce a current in the adjoining helix. It was found that the galvanometer needle indicated a current at the moment both of completing and breaking the circuit, but that in the interval no deflection took place; and similarly the induced currents readily magnetized a sewing needle, while the electric current along the inducing helix was in the act of beginning or ceasing to flow, but at no other period. By varying the experiment the same result was obtained; an electric current transmitted from a voltaic battery through a conducting helix does not induce a current in an adjoining helix, except at the moment of making or breaking the voltaic circuit. In the former case the direction of the induced current is opposite to that of the inducing current, and in the latter case it is the same. This phenomenon is distinguished by Faraday under the name of *Volta-electric induction.*

Fig. 34.



The inducing power of a magnet greatly exceeds that of an electric current. A ring of soft iron was covered to nearly half its extent by several helices, the ends of which were brought together so as to constitute a compound helix terminating in the conductors *a b*, figure 34; and on the other half of the ring were arranged similar helices which communicated by *c d* with a galvanometer. The two sets of helices were thus separated from each other by portions of the ring M M′, and were protected by cloth from direct contact with the ring itself. At the moment the wires *a b* touched the ends of a voltaic combination, the galvanometer was strongly affected: the needle then returned to its former position and remained there until the voltaic circuit was broken, when the needle was again deflected as strongly as before, but in the opposite direction. The action was still greater when both compound helices were on the same part of the ring, the induction being increased apparently by the closer contiguity of the helices. Another of Faraday's arrangements, which was in several respects more convenient than the ring, consisted of a hollow cylinder of pasteboard, round which two compound helices were adjusted. On connecting one helix with a voltaic combination, the other deflected the galvanometer and magnetized a needle, as in the experiments of volta-electric induction at first described; but when a cylinder of soft iron was introduced into the pasteboard case, and a voltaic current transmitted as before, the effect on the galvanometer was much greater. The action in this last experiment and with the iron ring is distinguished by the name of *Magneto-electric induction.*

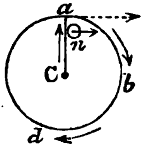
The phenomena arising from magneto-electric and volta-electric induction are manifestly owing to the same condition of the induced wire: the action on the needle, though different in force, is identical in kind. It is equally clear that the agent brought into operation in the induced wire is an electric current, or, to dismiss the language of theory, that the induced wire is in the same electric state as the conducting wire in a closed voltaic circle. Its power in magnetizing steel and deflecting a magnet is sufficient evidence of this; but Faraday, by magneto-electric induction, succeeded in throwing a frog's leg into spasms by connecting it with the induced wire; and by arming the ends of that wire with points of charcoal, and separating them at the instant the galvanic circuit of the inducing wire was broken or restored, sparks of electricity were obtained. The mode in which soft iron contributes to the effect is likewise obvious. An electric current circulating round a bar of soft iron has been shown to convert it into a temporary magnet possessed of surprising power (page 114); and it is doubtless to this magnet, called into temporary existence by the electric current, most of the induced electricity is to be ascribed. Faraday reduced this to certainty by surrounding a cylinder of soft iron with one helix connected with the galvanometer, and converting the soft iron into a temporary magnet, not by a voltaic battery, but by placing at each end of the cylinder the opposite pole of a magnet. During the act of applying the magnetic poles to the iron, the galvanometer needle was deflected; and the deflection was reproduced, but in the opposite direction, when the magnetism of the iron was ceasing by the removal of the magnet. Similarly when a helix was wound on a hollow cylinder of pasteboard, and a real magnet was introduced, the galvanometer was deflected: the needle then remained quiescent so long as the magnet was left in the cylinder; but in the act of its removal, the needle was again deflected, though as usual in the opposite direction.

These singular phenomena, which establish such new and intimate relations between voltaic and magnetic action, and supply additional evidence in favour of Ampère's beautiful theory of magnetism, have led to an experiment by which, at first view, an electric spark appeared to be derived from the magnet itself. After Faraday had announced his experiment, above mentioned, of obtaining a spark from the induced wire, other attempts were made to effect the same object with a magnet, without the aid of galvanism. The first person who succeeded in this country was Professor Forbes, who operated with a powerful loadstone which had been presented to the University of Edinburgh by Dr. Hope. (Phil. Trans. of Ed. 1832.) A helix of copper wire was formed round the middle of a cylinder of soft iron, which was of such length that its extremities reached from one pole of the loadstone to the other. On applying and withdrawing the soft iron cylinder to and from the poles of the loadstone, magnetism was alternately created and destroyed within it. At these periods of transition, electric currents were induced in the helix surrounding the soft iron; and when, at these instants, metallic contact between the conducting wires of the helix was broken, an electric spark was visible. Mr. Forbes succeeded best by connecting one wire with a cup of mercury, and removing the other wire from contact with its surface at the instant when an assistant withdrew the armature of soft iron from the loadstone. In this experiment, therefore, the electricity was obtained from the helix, and was induced in it by the soft iron while in the act of acquiring or losing magnetism. The same experiment was performed by Mr. Faraday with a loadstone belonging to Professor Daniell; and shortly before the experiment of Mr. Forbes, Nobili and Antinori succeeded with an ordinary steel magnet. Pixii in Paris afterwards performed this experiment with great effect by causing a strong horse-shoe magnet to revolve upon an axis, its poles passing in rapid succession in front of a soft iron armature of the same form; and a still better arrangement is to cause the armature to revolve in front of the poles of a powerful magnet, as in the instrument fitted up by Mr. Saxton, and exhibited at the Adelaide-rooms, London. The voltaic currents are induced in one direction as the armature approaches the magnetic poles, and are reversed as it quits them; so that the currents change their direction twice in each revolution. On all these occasions the source of the electricity is the same, being always induced in the helix by a temporary magnet; and it has all the characters of a voltaic current. It produces brilliant sparks, renders platinum wire red-hot, and gives a strong shock. It readily explodes gunpowder; and Dr. Ritchie has fitted up an apparatus for exploding with it a mixture of oxygen and hydrogen gases. It decomposes water rapidly; and though from the rapid reversal in the direction of the currents, both gases are given off at the same wire, Pixii succeeded in collecting them separately. (An. de Ch. et de Ph. li. 72.)

Intimately associated with magneto-electric induction, if not referable to the very same origin, is the induction of electric currents by movement. On introducing a magnet into a hollow helix of copper wire, as also on withdrawing the magnet after its introduction, an electric current was momentarily induced in the wire; and if, the magnet being stationary, the helix were moved in its vicinity, an electric current is likewise induced. The action is not confined to magnets and copper wire; but in all solid conductors of electricity, when moved near the pole of a magnet, an electric current is generated, and the most perfect conductors act with the greatest effect. The direction of the movement is not immaterial: it is essential that the plane in which the conductor moves should form an angle with the axis of the magnet; and the most powerful currents were induced, when the plane of motion was at right angles to that axis, and hence parallel to the electric currents which Ampère supposes to exist in the magnet. The direction of the currents depends on the direction of motion. If the movement of a wire from right to left cause a certain current, an opposite current will be induced when the wire is moved from left to right. In short, with regard to the direction of an induced current, Mr. Faraday's researches establish this law, deduced by Dr. Ritchie: if a wire, conducting voltaic electricity, produce on magnets or conductors certain motions, whether repulsive, attractive, or rotatory; and if the battery be removed, the ends of the wires brought into metallic contact, and the same motions be produced by mechanical means, the conductor will have the same electric state induced in it as it had when connected with the battery. (Phil. Mag. 3rd series, iv. 12.)

Mr. Faraday has applied this principle in a most happy manner to explain the phenomena of rotation discovered by M. Arago. If a plate of copper be revolved close to a magnetic needle suspended so that it may rotate in a plane parallel to the plate, the needle will rotate in the same direction; and, reciprocally, a rotating magnet tends to give rotation to a contiguous copper plate. The same effects are produced by the rotation not only of all metals, but, according to Arago, of all bodies, whether solid, liquid, or gaseous. These effects, which Faraday has principally examined in reference to the rotation of metals, are entirely owing to electric currents induced by the rotation, and flowing at right angles to the direction of motion. Suppose *a b d*, figure 35, to be a circular metallic plate, placed horizontally, and capable of revolving round its centre *c*; and let *n* be the north pole of a magnet situated above the plate near its circumference at *a*. If a positive electric current were to flow along the plate from *c* to *a*, the pole *n* would be impelled at right angles in the direction indicated by the arrow; and hence if the plate were made to revolve in the same direction, indicated by the arrows at *b* and *d*, an induced positive current would instantly flow from *c* to *a*. Its direction would be constantly in that line, being at right angles to the dotted arrow, which indicates the direction in which that part of the plate nearest to the pole is moving. Hence the pole, acted on by the induced current, would receive an impulse in the same direction.

Fig. 35.



If motion in the vicinity of a magnet induce an electric current, the same effect would be anticipated from the magnetic influence of the earth; and this fact has been proved by Mr. Faraday by most decisive and interesting experiments. When a bar of soft iron is held in the position of the dipping needle, the direction of which, in regard to terrestrial magnetism, is analogous to the axis of a common magnet, it acquires magnetic properties; and, accordingly, on introducing a soft iron cylinder into a hollow helix of copper placed in the line of the dip, a galvanometer connected with the helix was instantly affected. But the use of iron may be dispensed with altogether; for when a helix of copper wire was simply moved at right angles to the dipping needle, electric currents were induced by the magnetism of the earth. The form of a helix is not even necessary: the movement of a piece of copper wire across the line of dip developed currents in the wire. The same effect was produced by the rotation of a copper plate placed horizontally so as to be nearly at right angles to the line of dip; and the revolution of a copper globe acted in the same manner. Faraday concludes that the rotation of the earth on its axis ought similarly to influence the conducting matters of its surface; and that electric currents should be thereby induced from the equatorial regions to either pole. He throws out the suggestion whether the aurora borealis and australis may not be produced by the returning currents passing from the poles of the earth into the atmosphere.

PART II.

INORGANIC CHEMISTRY.

PRELIMINARY REMARKS.

In teaching a science such as chemistry, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery, and proceed from individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss general principles in the first instance, in order to aid the beginner in remembering insulated facts, and in comprehending the explanations connected with them. I shall, accordingly, commence the second part of the work by explaining the leading doctrines of the science. One inconvenience, indeed, arises from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and, therefore, on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance, its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances it is applied to uses still more important. The character called *specific gravity*, the meaning of which was explained at page 48, is of so much importance that the mode of determining it will be mentioned in this place. The process consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weigh 9 grains, and the same bulk of another body 20 grains, its specific gravity is determined by this formula:—as 9 : 20 : : 1 (assumed as the specific gravity of water) to the fourth proportional 2.2222; so that the specific gravity of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them.* The method of obtaining the necessary data in case of a solid is somewhat different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference between the two weights gives the weight of a quantity of water equal to the bulk of the solid. This rule is founded on the hydrostatic law, that a solid body, immersed in any liquid, not only weighs less than it does in air, but the difference corresponds exactly to the weight of liquid which it displaces; and it is obvious that the liquid so displaced is exactly of the same dimensions as the solid. Another method is by the use of the bottle recommended for taking the specific gravity of liquids. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after its outer surface is made perfectly dry.

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* Bottles are prepared for this purpose by the philosophical instrument makers.

The determination of the specific gravity of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and, therefore, atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the observation of Dr. Prout, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60° F. and when the barometer stands at 30 inches, weigh 31.0117 grains. By a similar method the weight of any other gas may be determined, and its specific gravity be inferred accordingly. For instance, suppose 100 cubic inches of oxygen gas are found to weigh 34.109 grains, its specific gravity will be thus deduced; as 31.0117 : 34.109 : : 1 (the sp. gr. of air) : 1.1025, the specific gravity of oxygen.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases:—

1. The gas should be perfectly pure, otherwise the result cannot be accurate.

2. Due regard must be had to its hygrometric condition. If it is saturated with moisture, the necessary correction may be made by the formula of page 50; or it may be dried by the use of substances which have a powerful attraction for moisture, such as chloride of calcium, quicklime, or fused potassa.

3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations admit of comparison, unless made under the same elevation of the barometer. It is always understood, in taking the specific gravity of a gas, that the barometer must stand at thirty inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is, therefore, called the standard height; and if the mercurial column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by careful experiment, that the bulk of gases is inversely as the pressure to which they are subject. Thus, 100 measures of air, under the pressure of a thirty-inch column of mercury, will dilate to 200 measures, if the pressure be diminished by one-half; and will be compressed to fifty measures, when the pressure is double, or equal to a mercurial column of sixty inches. The correction for the effect of pressure may, therefore, be made by the rule of three, as will appear by an example. If a certain portion of gas occupy the space of 100 measures at twenty-nine inches of the barometer, its bulk at thirty inches may be obtained by the following proportion; as 30 : 29 : : 100 : 96.66. It is understood that the temperature of the mercurial column is constant; if not so, correction must be made agreeably to the note at page 18.

For a similar reason the temperature should always be the same. The standard or mean temperature is 60°; and if the gas be admitted into the weighing-flask when the thermometer is above or below that point, the formula of page 21 should be employed for making the necessary correction.

Chemistry is indebted for its nomenclature to the labours of four celebrated chemists, Lavoisier, Berthollet, Guyton-Morveau, and Fourcroy. The principles which guided them in its construction are exceedingly simple and ingenious. The known elementary substances, and the more familiar compound ones, were allowed to retain the appellation which general usage had assigned to them. The newly-discovered elements were named from some striking property. Thus, as it was supposed that acidity was always owing to the presence of the vital air discovered by Priestley and Scheele, they gave it the name of *oxygen*, from ὀξυς acid, and γενναν to generate; and they called inflammable air *hydrogen*, from ὕδωρ water, and γενναν, because it enters into the composition of water.

Compounds, of which oxygen forms a part, were called *acids* or *oxides*, according as they do or do not possess acidity. An oxide of iron or copper signifies a combination of those metals with oxygen, which has no acid properties. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus, sulphur*ic* and carbon*ic* acids signify acid compounds of sulphur and carbon with oxygen. If sulphur or any other body should form two acids, that which contains the least quantity of oxygen is made to terminate in *ous*, as sulphur*ous* acid. The termination in *uret* was intended to denote combinations of the simple non-metallic substances either with one another, with a metal, or with a metallic oxide. Sulph*uret* and carb*uret* of iron, for example, signify compounds of sulphur and carbon with iron. The different oxides or sulphurets of the same substance were distinguished from one another by some epithet, which was commonly derived from the colour of the compound, such as the black and red oxides of iron, the black and red sulphurets of mercury. Though this practice is still continued occasionally, it is now more customary to distinguish degrees of oxidation by the use of derivatives from the Greek or Latin. *Prot*oxide signifies the first degree of oxidation, *bin*oxide the second, and *ter*oxide the third; and the term *per*oxide is often applied to the highest degree of oxidation. The Latin word *sesqui*, one and a half, is used as an affix when the elements of an oxide are as 1 to 1½, or as 2 to 3. The sulphurets, carburets, &c. of the same substance are designated in a similar way. Compounds consisting of acids in combination with metallic oxides, or any alkaline bases, are termed *salts*, the names of which are so contrived as to indicate the substances contained in them. If the acidified substance contain a maximum of oxygen, the name of the salt terminates in *ate*; if a minimum, the termination in *ite* is employed. Thus, the sulph*ate*, phosph*ate*, and arseni*ate* of potassa, are salts of sulphur*ic*, phosphor*ic*, and arsen*ic* acids; while the terms sulph*ite*, phosph*ite*, and arsen*ite* of potassa, denote combinations of that alkali with the sulphur*ous*, phosphor*ous*, and arseni*ous* acids.

The advantage of a nomenclature which disposes the different parts of a science in so systematic an order, and gives such powerful assistance to the memory, is incalculable. The principle has been acknowledged in all countries where chemical science is cultivated, and its minutest details have been adopted in Britain. It must be admitted, indeed, that in some respects the nomenclature is defective. The erroneous idea of oxygen being the general acidifying principle, has exercised an injurious influence over the whole structure. It would have been convenient also to have had a different name for hydrogen. But it is now too late to attempt a change; for the confusion attending such an innovation would more than counterbalance its advantages. The original nomenclature has, therefore, been preserved, and such additions have been made to it as the progress of the science rendered necessary. The most essential improvement was suggested by the discovery of the laws of chemical combination. The different salts formed of the same constituents were formerly divided into *neutral*, *super*, and *sub*-salts. They were called neutral if the acid and alkali were in such proportion that one neutralized the other; super-salts, if the acid prevailed; and sub-salts, if the alkali was in excess. The name is now regulated by the atomic constitution of the salt. If it is a compound of an equivalent of the acid and the alkali, the generic name of the salt is employed without any other addition; but if two or more equivalents of the acid are attached to one of the base, or two or more equivalents of the base to one of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potassa are called sulphate and *bi*sulphate; the first containing an equivalent of the acid and the alkali, and the second salt, two of the former to one of the latter. The three salts of oxalic acid and potassa are termed the oxalate, *bin*oxalate, and *quadr*oxalate of potassa; because one equivalent of the alkali is united with one equivalent of acid in the first, with two in the second, and with four in the third salt. As the numerals which denote the equivalents of the acid in a super-salt are derived from the Latin language, Dr. Thomson proposes to employ the Greek numerals, *dis*, *tris*, *tetrakis*, to signify the equivalents of alkali in a sub-salt; and I shall not only adopt his proposition, but give it the following extension. Since, agreeably to the electro-chemical theory, the elements of a compound may in relation to each other be considered oppositely electric, I shall distinguish two or more equivalents of the negative element by Latin numerals, and apply Greek numerals to that element which is regarded as positive. Thus a *bi*chloride denotes a compound which contains two equivalents of the negative element chlorine; whereas a *di*chloride indicates that one equivalent of chlorine is combined with two of some positive body.

SECTION I.

AFFINITY.

All chemical phenomena are owing to Affinity or Chemical Attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence it forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances; in other words, apparent contact, or the closest proximity, is necessary to its action. Every thing which prevents such contiguity is an obstacle to combination; and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the former case, they do not come within the sphere of their mutual attraction; in the latter, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power distinct from the other forces which act on matter, its action may be promoted, modified, or counteracted by them; and consequently, in studying the phenomena produced by affinity, it is necessary to inquire into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the admixture of two substances. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with sulphuric ether, and still less with oil; for however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in a very small degree by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all; between some substances it acts very feebly, and between others with great energy.

Simple combination of two substances is a common occurrence; of which the solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances. But the phenomena are often more complex. The formation of a new compound is often attended by the destruction of a pre-existing one; as when some third body acts on a compound, for one element of which it has a greater affinity than they have for one another. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence if this acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free, because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from nitric acid. Combination and decomposition occur in each of these cases;—combination of sulphuric acid with ammonia, of water with alcohol, and of baryta with sulphuric acid;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, and of nitric acid and baryta. These are examples of what Bergmann called *single elective affinity;*—elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables, of which the following, drawn up by Geoffroy, is an example:—

Sulphuric acid.

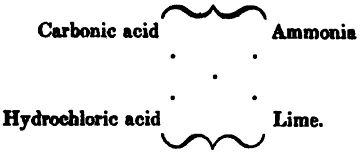
Baryta,
Strontia,
Potassa,
Soda,
Lime,
Ammonia,
Magnesia.

This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and may unite separately with each; and, secondly, that the base of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus ammonia will separate magnesia, lime ammonia, and potassa lime; but none can withdraw baryta from sulphuric acid, nor can ammonia or magnesia decompose sulphate of lime, though strontia or baryta will do so. Bergmann conceived that these decompositions are solely determined by chemical attraction, and that consequently the order of decomposition represents the comparative forces of affinity; and this view, from the simple and natural explanation it affords of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime separates ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that ammonia may in reality have a stronger attraction for sulphuric acid than lime, and yet that the latter, from the great influence of disturbing causes, may succeed in decomposing sulphate of ammonia.

The propriety of the foregoing remark will be made obvious by the following example. When a stream of hydrogen gas is passed over oxide of iron heated to redness, the oxide is reduced to the metallic state, and water is generated. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that hydrogen has a stronger attraction than iron for oxygen; and from that of the second, that iron has a greater affinity for oxygen than hydrogen. But these inferences are incompatible with each other. The affinity of oxygen for the two elements, hydrogen and iron, must either be equal or unequal. If equal, the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. But if the forces are unequal, the decomposition in one of the experiments must have been determined by extraneous causes, in direct opposition to the tendency of affinity.

To Berthollet is due the honour of pointing out the fallacy of Bergmann's opinion. He was the first to show that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of the mode in which they operate. Berthollet went even a step further. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another; he maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher went too far. Bergmann erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy is, I apprehend, indisputable. Water has a much greater affinity for hydrochloric acid and ammoniacal gases than for carbonic and hydrosulphuric acids, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of hydrosulphuric acid by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of still more complicated changes than those which have been just considered. In a case of single elective affinity, three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances may be studied by aid of a diagram, a method which was first employed, I believe, by Dr. Black, and has since been generally practised. Thus, in mixing together a solution of carbonate of ammonia and hydrochlorate of lime, their mutual action may be represented in the following manner:



Each of the acids has an attraction for both bases, and hence it is possible either that the two salts should continue as they were, or that an interchange of principles should ensue, giving rise to two new compounds—carbonate of lime and hydrochlorate of ammonia. According to the views of Bergmann, the result is solely dependent on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of hydrochloric acid for lime, exceed that of carbonic acid for lime, added to that of hydrochloric acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called *double elective affinity*. Mr. Kirwan applied the terms *quiescent* and *divellent* to denote the tendency of the opposing affinities, the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single elective attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if carbonate of ammonia decompose hydrochlorate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose hydrochlorate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and hydrochlorate of lime being formed; and, therefore, if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by hydrosulphuric acid gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

CHANGES THAT ACCOMPANY CHEMICAL ACTION.

The leading circumstance that characterizes chemical action is the loss of properties experienced by the combining substances, and the acquisition of new ones by the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognizing their presence. But more generally the properties of one or both of the combining bodies disappear entirely. One would not suppose from its appearance that water is a compound body; much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire; oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalies and earths were regarded as simple till Sir H. Davy proved them to be compound, and certainly they evince no sign whatever of containing oxygen and a metal. Numerous examples of a similar kind are afforded by the mutual action of acids and alkalies. Sulphuric acid and potassa, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances; the latter has a pungent taste, converts the blue colour of vegetables to green, and combines readily with acids. On adding these principles cautiously to each other, a compound results called a *neutral salt*, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to *neutralize* one another.

The other phenomena that accompany chemical action are changes of density, temperature, form, and colour.

1. It is observed that two bodies rarely occupy, after combination, the same space which they possessed separately. In general their bulk is diminished, so that the specific gravity of the new body is greater than the mean of its components. Thus a mixture of 100 measures of water and an

equal quantity of sulphuric acid does not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metalic compounds; and there are examples of combination between gases without any change of bulk.

2. A change of temperature generally accompanies chemical action. Heat is evolved either when there is a diminution in the bulk of the combining substances without change of form, or when a gas is condensed into a liquid, or a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slaking lime, during which water loses its liquid form in combining with that earth, is an example of the latter. The rise of temperature in these cases is obviously referable to diminution in the capacity of the new compound for heat; but intense heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of specific heat is quite inadmissible. At present it is enough to have stated the fact; its theory will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when heat is rendered insensible by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. The changes of form that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, and liquids solid. Several familiar chemical phenomena, such as detonation, effervescence, and precipitation, are owing to these changes. The sudden evolution of a large quantity of gaseous matter causes an explosion, as when gunpowder detonates. The slower disengagement of gas produces effervescence, as when marble is put into hydrochloric acid. A precipitate is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved.

4. Chemical action is frequently attended by change of colour. No uniform relation has been traced between the colour of a compound and that of its elements. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The brown oxide of copper generally gives rise to green and blue coloured salts; while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a very important study, as it supplies a character by which most substances may be distinguished.

CIRCUMSTANCES THAT MODIFY AND INFLUENCE THE OPERATION OF AFFINITY.

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important;—cohesion, elasticity, quantity of matter, and gravity. To these may be added the agency of the imponderables.

Cohesion.—The first obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. For this reason, bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and, therefore, combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways, by mechanical division, or by the application of heat. The former is useful by increasing the extent of surface; but it is not of itself in general sufficient, because the particles, however minute, still retain that degree of cohesion which constitutes *solidity*. Heat acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. The fluidity of one of the substances frequently suffices for effecting chemical union, as is proved by the facility with which water dissolves many salts and other solid bodies. But the cohesive force is still in operation; for a solid is commonly dissolved in greater quantity when its cohesion is diminished by heat. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their cohesive power is still further diminished. It seems fair to infer, therefore, that very little, if any, affinity exists between two bodies which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendancy of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, part of the saline matter generally separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together and are deposited in crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt, therefore, assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on mixing together a solution of two acids and one alkali, of which two salts may be formed, one soluble, and the other insoluble, the alkali will unite with that acid with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and is certainly applicable to many of the instances to be found in the tables of affinity. When, for example, hydrochloric acid, sulphuric acid, and baryta, are mixed together, sulphate of baryta is formed in consequence of its insolubility. Lime, which yields an insoluble salt with carbonic acid, separates that acid from ammonia, potassa, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. On mixing together in solution four substances, A, B, C, D, of which it is possible to form four compounds, AB and CD, or AC and BD, that compound will certainly be produced, which happens to be insoluble. Thus sulphuric acid, soda, nitric acid, and baryta, may give rise either to sulphate of soda and nitrate of baryta, or to sulphate of baryta and nitrate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly generated, and its formation necessarily causes the nitric acid to combine with the soda. In like manner, a solution of nitrate of lime is decomposed by carbonate of ammonia, in consequence of the insolubility of carbonate of lime.

To comprehend the manner in which cohesion acts in these instances, it is necessary to consider what takes place when in the same liquid two or more compounds are brought together, which do not give rise to an insoluble substance. Thus on mixing solutions of sulphate of potassa and nitrate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and nitrate of potassa, are likewise soluble. In this case it is possible either that each acid may be confined to one base, so as to constitute two neutral salts; or that each acid may be divided between both bases, yielding four neutral salts. It is difficult to decide this point in an unequivocal manner: but judging from many chemical phenomena, there can, I apprehend, be no doubt that the arrangement last mentioned is the most frequent, and is probably universal whenever the relative forces of affinity are not very unequal. When two acids and two bases meet together in neutralizing proportion, it may, therefore, be inferred, that each acid unites with both the bases in a manner regulated by their respective forces of affinity, and that four salts are contained in solution. In like manner the presence of three acids and three bases will give rise to nine salts; and when four of each are present, sixteen salts will be produced. This view affords the most plausible theory of the constitution of mineral waters, and of the products which they yield by evaporation.

The influence of insolubility in determining the result of chemical action may be readily explained on this principle. If nitric acid, sulphuric acid, and baryta, are mixed together in solution, the base may be conceived to be at first divided between the two acids, and nitrate and sulphate of baryta to be generated. The latter being insoluble is instantly removed beyond the influence of the nitric acid, so that for an instant nitrate of baryta and free sulphuric acid remain in the liquid; but as the base left in solution is again divided between the two acids, a fresh quantity of the insoluble sulphate is generated; and this process of partition continues, until either the baryta or the sulphuric acid is withdrawn from the solution. Similar changes ensue when nitrate of baryta and sulphate of soda are mixed.

The separation of salts by crystallization from mineral waters or other saline mixtures is explicable by a similar mode of reasoning. Thus on mixing nitrate of potassa and sulphate of soda, four salts, according to this view, are generated, namely, the sulphates of soda and potassa, and the nitrates of those bases; and if the solution be allowed to evaporate gradually, a point at length arrives when the least soluble of these salts, the sulphate of potassa, will be disposed to crystallize. As soon as some of its crystals are deposited, and thus withdrawn from the influence of the other salts, the constituents of these undergo a new arrangement, whereby an additional quantity of sulphate of potassa is generated; and this process continues until the greater part of the sulphuric acid and potassa has combined, and the compound is removed by crystallization. If the difference in solubility is considerable, the separation of salts may be often rendered very complete by this method.

The efflorescence of a salt is sometimes attended with a similar result. If carbonate of soda and chloride of calcium are mingled together in solution, the insoluble carbonate of lime subsides. But if carbonate of lime and sea-salt are mixed in the solid state, and a certain degree of moisture is present, carbonate of soda and chloride of calcium are slowly generated; and since the former, as soon as it is formed, separates itself from the mixture by efflorescence, its production continues progressively. The efflorescence of carbonate of soda, which is sometimes seen on old walls, or which in some countries is found on the soil, appears to have originated in this manner.

Elasticity.—From the obstacle which cohesion puts in the way of affinity, the gaseous state, in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen gases, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. This want of action seems to arise from the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many gases cannot be made to unite directly, which nevertheless combine readily while in their *nascent* state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, the reciprocal attraction of which is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. Chloride of nitrogen, which is an oil-like liquid, composed of the two gases chlorine and nitrogen, affords an apt illustration of this principle, being distinguished for its remarkable facility of decomposition. Slight elevation of temperature, by increasing the natural elasticity of the two gases, or contact of substances which have an affinity for either of them, produces immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle, are liable to be decomposed by a high temperature. The expansion occasioned by heat removes the elements of the compound to a greater distance from each other, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances, which contain water in a state of intimate combination, part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

From these and some preceding remarks, it appears that the influence of heat over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, heat favours affinity either by diminishing the cohesion of a solid, or by converting it into a liquid. As the cause of the gaseous state, on the contrary, it keeps at a distance particles which would otherwise unite; or, by producing expansion, it tends to separate from one another substances which are already combined. There is one effect of heat which seems somewhat anomalous; namely, the combination which ensues in gaseous explosive mixtures on the approach of flame. The explanation given by Berthollet is probably correct, —that the sudden dilatation of the gases in the immediate vicinity of the flame, acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third body, the last will, in general, be completely driven off by the application of heat. The decomposition of the salts of ammonia by the pure alkalies or alkaline earths, may be adduced as an example; and for the same reason, all the carbonates are decomposed by hydrochloric acid, and all the hydrochlorates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why the dry carbonate of lime will decompose hydrochlorate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the hydrochlorate either of ammonia or lime.

The influence of elasticity in determining the result of chemical action in these instances, seems owing to the same cause which enables insolubility to be productive of similar effects. Thus, on mixing hydrochlorate of ammonia with lime, the acid is divided between the two bases; some ammonia becomes free, which, in consequence of its elasticity, is entirely expelled by a gentle heat. The acid of the remaining hydrochlorate of ammonia is again divided between the two bases; and if a sufficient quantity of lime is present, the ammoniacal salt will be completely decomposed. In like manner the decomposition of potassa may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potassa in the fused state be brought in contact with metallic iron at a white heat, the oxygen is divided between the two metals, and a portion of potassium set at liberty. But as potassium is volatile at a white heat, it is expelled at the instant of reduction; and thus, by its influence being withdrawn, an opportunity is given for the decomposition of an additional quantity of potassa.

ıtity of Matter. The influence of quantity of matter over affinity is ally admitted. If one body A unites with another body B in several ions, that compound will be most difficult of decomposition which s the smallest quantity of B. Of the three oxides of lead, for instance, roxide parts most easily with its oxygen by the action of heat; a temperature is required to decompose the red oxide; and the de will bear the strongest heat of our furnaces without losing a of its oxygen.

influence of quantity over chemical attraction may be further illus- ›y the phenomena of solution. When equal weights of a soluble salt ed in succession to a given quantity of water, which is capable of ng almost the whole of the salt employed, the first portion of the salt appear more readily than the second, the second than the third, the ıan the fourth, and so on. The affinity of the water for the saline ıce diminishes with each addition, till at last it is weakened to such a as to be unable to overcome the cohesion of the salt. The process ases, and a saturated solution is obtained.

ıtity of matter is employed advantageously in many chemical opera- If, for instance, a chemist is desirous of separating an acid from a c oxide by means of the superior affinity of potassa for the former, he tly uses rather more of the alkali than is sufficient for neutralizing d. He takes the precaution of employing an excess of alkali, in order re effectually to bring every particle of the substance to be decomposed act with the decomposing agent.

Berthollet has attributed a much greater influence to quantity of mat- t was the basis of his doctrine, developed in the *Statique Chimique*, dies cannot be wholly separated from each other by the affinity of a ubstance for one element of a compound; and to explain why a su- chemical attraction does not produce the effect which might be ex- from it, he contended that quantity of matter compensates for a weaker . From the co-operation of several disturbing causes, Berthollet per- that the force of affinity cannot be estimated with certainty by observ- order of decomposition; and he, therefore, had recourse to another l. He set out by supposing that the affinity of different acids for the lkali, is in the inverse ratio of the ponderable quantity of each which ssary for neutralizing equal quantities of the alkali. Thus, if two parts acid A, and one part of another acid B, are required to neutralize equal ies of the alkali C, it was inferred that the affinity of B for C was twice ıt as that of A. He conceived, further, that as two parts of A produce ne neutralizing effect as one part of B, the attraction exerted by any owards two parts of A ought to be precisely the same as for the one B; and he hence concluded that there is no reason why the alkali prefer the small quantity of one to the large quantity of the other. On founded the principle that quantity of matter compensates for force of on.

ıollet has here obviously confounded two things, namely, force of at- and neutralizing power, which are really different, and ought to be tinct. The relative weights of hydrochloric and sulphuric acids re- o neutralize an equal quantity of any alkali, or, in other words, their es of saturation, are as 36.4 to 40, a ratio which remains constant with to all other alkalies. The affinity of these acids, according to Ber- rule, will be expressed by the same numbers. But in taking this , we have to make three assumptions, each of which is disputable. no proof, in the first place, that hydrochloric acid has a greater af- an alkali, such as potassa, than sulphuric acid. Such an inference directly opposed to the general opinion founded on the order of de- ion; and though that order, as we have shown, is by no means a ıry test of the strength of affinity, it would be improper to adopt an conclusion without having good reasons for so doing. Secondly, stablished that hydrochloric acid has the greater affinity, it does not follow that the attraction of those acids for potassa is in the ratio of 36.4 to 40. *And*, thirdly, supposing this point settled, it is very improbable that the ratio of their affinities for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, M. Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Gravity.—The influence of gravity is perceptible when it is wished to make two substances unite, the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ from one another in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound; unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

Imponderables.—The influence which heat exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work. Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and, therefore, on the same principle as flame.

MEASURE OF AFFINITY.

As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same principle, under the same circumstances, and subsequently by marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus, on exposing silver, lead, and iron, to air and moisture, the iron soon rusts, the lead is oxidized in a slight degree only, and the silver resists oxidation altogether. It is hence inferred that iron has the greatest affinity for oxygen, lead next, and silver the least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. Oxide of silver is reduced by heat only; and oxide of lead is decomposed by charcoal at a lower temperature than oxide of iron.

It is inferred from the action of heat on the carbonate of potassa, baryta, lime, and oxide of lead, that potassa has a stronger attraction for carbonic acid than baryta, baryta than lime, and lime than oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of acids and alkalies for each other is the most uncertain. Their action on one another is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both of them are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the former philosopher apply equally to that proposed by the latter. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

SECTION II.

PROPORTIONS IN WHICH BODIES UNITE, AND THE LAWS OF COMBINATION.

The study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those, the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, hydrochloric, and nitric acids, affords instances of the first mode of combination; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid; or they may be mixed together in any intermediate proportions; and nevertheless in each case they appear to unite perfectly with each other. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its solvent power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the cohesive power; and but for the obstacle which it occasions, the salt would most probably unite with water in every proportion.

All the substances that unite in many proportions, give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of minor importance; but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to each other under circumstances peculiarly favourable for acting with effect: the liquid form is thus communicated to them; while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their mutual attraction.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only; and which, in combining, lose more or less completely the properties that distinguish them when separate. Of these bodies, some form but one combination. Thus there is only one compound of boron and oxygen, and of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by tin and oxygen, and by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, except perhaps carbon and hydrogen, and those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by the three following remarkable laws:—

1. The first of these laws is, that the composition of bodies is fixed and invariable. A compound substance, so long as it retains its characteristic properties, always consists of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts* of the former to 24 of the latter: no other elements can form it, nor can it be produced by its own elements in any other proportion. Water, in like manner, is formed of 1 part of hydrogen

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* By the expression 'parts' I always mean parts by weight.

and 8 of oxygen; and were these two elements to unite in any other proportion, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus, sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 76.7 of baryta. This law, in fact, is universal and permanent. Its importance is equally manifest: it is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by Berthollet, in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same causes in producing the effect at present under consideration. Finding that the solubility of a salt and of a gas in water is limited, in the former by cohesion, and in the latter by elasticity, he conceived that the same forces would account for the unchangeable composition of certain compounds. He maintained, therefore, that within certain limits bodies have a tendency to unite in every proportion; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 76.7 of baryta, not because those substances are disposed to unite in that ratio rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions, which, if true, would shake the whole science of chemistry to its foundation, were founded on observation and experiment, supported by all the ingenuity of that highly gifted philosopher. They were ably and successfully combated by Proust in several papers published in the *Journal de Physique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable. The controversy which ensued between these eminent chemists, is remarkable for the moderation with which it was conducted on both sides, and has been properly quoted by Berzelius as a model to controversialists. How much soever opinion may have been divided upon the question at that period, the controversy is now at an end. The great variety of new facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by the phenomena of solution, are rather apparent than real; for it is conceivable that the apparent variety of proportion, noticed in such cases, may arise from the mixture or combination of a few definite compounds with each other.

2. The second law of combination is, that the relative quantities in which bodies unite may be expressed by proportional numbers. Thus, 8 parts of oxygen unite with 1 part of hydrogen, 16 of sulphur, 35.4 of chlorine, 39.6 of selenium, and 108 parts of silver. Such are the quantities of these five bodies which are disposed to unite with 8 parts of oxygen; and it is found that when they combine with one another, they unite either in the proportions expressed by those numbers, or in multiples of them according to the third law of combination. Hydrosulphuric acid, for instance, is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuret of hydrogen of 1 part of hydrogen to 32 of sulphur; 35.4 of chlorine unite with 1 of hydro-

gen, 16 of sulphur, and 108 of silver; and 39.6 parts of selenium with 1 of hydrogen, and 16 of sulphur.

From the occurrence of such proportional numbers has arisen the use of certain terms, as *Proportion*, *Combining Proportion*, *Proportional*, and *Chemical Equivalent*, or *Equivalent*, to express them. The latter term, introduced by Dr. Wollaston, and which I shall commonly employ, was suggested by the circumstance that the combining proportion of one body is, as it were, equivalent to that of another body, and may be substituted for it in combination. At page 141 will be found a table of the equivalents of elementary substances.

This law does not apply to elementary substances only, since compound bodies have their combining proportions or equivalents, which may likewise be expressed in numbers. Thus, since water is composed of one equivalent or 8 parts of oxygen, and one equivalent or 1 of hydrogen, its combining proportion or equivalent is 9. The equivalent of sulphuric acid is 40, because it is a compound of one equivalent or 16 parts of sulphur, and three equivalents or 24 parts of oxygen; and in like manner, the combining proportion of hydrochloric acid is 36.4, because it is a compound of one equivalent or 35.4 parts of chlorine, and one equivalent or 1 part of hydrogen. The equivalent number of potassium is 39, and as that quantity combines with 8 of oxygen to form potassa, the equivalent of the latter is $39+8=47$. Now when these compounds unite, one equivalent of the one combines with one, two, three, or more equivalents of the other, precisely as the simple substances do. The hydrate of potassa, for example, is constituted of 47 parts of potassa and 9 of water, and its equivalent is consequently $47+9$, or 56. The sulphate of potassa is composed of 40 sulphuric acid+47 potassa; and the nitrate of the same alkali of 54 nitric acid+47 of potassa. The equivalent of the former salt is, therefore, 87, and of the latter 101.

The composition of the salts affords a very instructive illustration of this subject; and to exemplify it still further, a list of the equivalents of a few acids and alkaline bases is annexed:—

Hydrofluoric acid	19.7	Lithia	18
Phosphoric acid	35.7	Magnesia	20.7
Hydrochloric acid	36.4	Lime	28.5
Sulphuric acid	40	Soda	31.3
Nitric acid	54	Potassa	47
Arsenic acid	57.7	Strontia	51.8
Selenic acid	63.6	Baryta	76.7

It will be seen at a glance that the neutralizing power of the different alkalies is very different; for the equivalent of each base expresses the quantity required to neutralize an equivalent of each of the acids. Thus 18 of lithia, 31.3 of soda, and 76.7 of baryta, combine with 54 of nitric acid, forming the neutral nitrates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 35.7 of phosphoric, 40 of sulphuric, and 57.7 of arsenic acid unite with 76.7 of baryta, forming a neutral phosphate, sulphate, and arseniate of baryta.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel; namely, that when two neutral salts mutually decompose each other, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 71.3 parts of neutral sulphate of soda are mixed with 130.7 of nitrate of baryta, the 76.7 parts of baryta unite with 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 31.3 of soda of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

Sulphate of Soda.		Nitrate of Baryta.	
Sulphuric acid	40	54	Nitric acid.
Soda . .	31.3	76.7	Baryta.
	71.3	130.7	

It matters not whether more or less than 71.3 parts of sulphate of soda are added; for if more, a small quantity of sulphate of soda will remain in solution; if less, nitrate of baryta will be in excess; but in either case the neutrality will be unaffected.

3. The third law of combination is, that when one body A unites with another body B in two or more proportions, the quantities of the latter, united with the same quantity of the former, bear to each other a very simple ratio. The progress of chemical research, in discovering new compounds and ascertaining their exact composition, has shown that these ratios of B may be represented by one or other of the two following series:—

1st Series. A unites with 1, 2, 3, 4, 5, &c. of B.
2d Series. A unites with, 1, 1½, 2, 2½, &c. of B.

The first series is exemplified by the subjoined compounds.—

Water is composed of	Hydrogen	1	Oxygen	8	1
Binoxide of hydrogen	Do.	1	Do.	16	2
Carbonic oxide	Carbon	6	Do.	8	1
Carbonic acid	Do.	6	Do.	16	2
Nitrous oxide	Nitrogen	14	Do.	8	1
Nitric oxide	Do.	14	Do.	16	2
Hyponitrous acid	Do.	14	Do.	24	3
Nitrous acid	Do.	14	Do.	32	4
Nitric acid	Do.	14	Do.	40	5

It is obvious that in all these compounds the ratios of the oxygen are expressed by whole numbers. In water the hydrogen is combined with half as much oxygen as in the binoxide of hydrogen, so that the ratio is as 1 to 2. The same relation holds in carbonic oxide and carbonic acid. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. In like manner the ratio of sulphur in the two sulphurets of mercury, and that of chlorine in the two chlorides of mercury, is as 1 to 2. So, in bicarbonate of potassa, the alkali is united with twice as much carbonic acid as in the carbonate; and the acid of the three oxalates of potassa is in the ratio of 1, 2, and 4.

The following compounds exemplify the second series:—

Protoxide of iron consists of	Iron	28	Oxygen	8	1
Peroxide	Do.	28	Do.	12	1½
Protoxide of manganese	Manganese	27.7	Do.	8	1
Sesquioxide	Do.	27.7	Do.	12	1½
Binoxide	Do.	27.7	Do.	16	2
Arsenious acid	Arsenic	37.7	Do.	12	1½
Arsenic acid	Do.	37.7	Do.	20	2½
Hypophosphorous acid	Phosphorus	15.7	Do.	4	½
Phosphorous acid	Do.	15.7	Do.	12	1½
Phosphoric acid	Do.	15.7	Do.	20	2½

Both of these series, which together constitute the third law of combination, result naturally from the operation of the second law. The first series arises from one equivalent of a body uniting with 1, 2, 3, or more equivalents of another body. The second series is a consequence of two equivalents of one substance combining with 3, 5, or more equivalents of another. Thus if two equivalents of phosphorus unite both with 3 and with 5 equivalents of oxygen, we obtain the ratio of 1½ to 2½; and should one equivalent of iron combine with one of oxygen, and another compound be formed of two equivalents of iron to three of oxygen, then the oxygen united with the same weight of iron would have the ratio, as in the table, of 1 to 1½. The compounds of manganese and phosphorus with oxygen afford examples of the same nature. Still more complex arrangements will be readily conceived, such as 3 equivalents of one substance to 4, 5, or more of another. But it is remarkable that combinations of the kind are very rare; and even their existence, though theoretically possible, has not been decidedly established. Even some of the compounds which are usually included in the second series belong properly to the first. The red oxide of lead, for instance, appears in its chemical relations not so much as a direct compound of lead and oxygen, but as a kind of salt formed by the union of the binoxide of lead with the protoxide of the same metal. On this supposition the two other oxides belong to the first series.

The merit of establishing the first law of combination seems justly due to Wenzel, a Saxon chemist; and the second law is also deducible from his experiments on the composition of the salts. His work, entitled *Lehre der Verwandtshaft*, was published in 1777. Bergmann and Richter, a few years after, confirmed the observations of Wenzel, though without adding materially in the way of generalization. The late Mr. Higgins, also, in 1789, speculated on the atomic constitution of compound bodies in a manner which, if pursued, would have led to the discovery of Dalton. It is to the latter, science is indebted for deducing from the scattered facts which had been previously collected, a theory of chemical union, embracing the whole science, and giving it a consistency and form which before his time it had never possessed. In his hands the second law of combination first attained its full generality; but the discovery which is more peculiarly his own, is that part of the third law of combination which is contained in the first of the two series above mentioned. The first public announcement of his views appears to have been made to the Philosophical Society of Manchester in 1803; and in 1808 they were explained in his New System of Chemical Philosophy. In the same year Dr. Wollaston and Dr. Thomson gave their evidence in support of the new doctrine, and other chemists have followed in the same path of inquiry. But of all who have successfully laboured in establishing the laws of combination, the most splendid contribution is that of the celebrated Berzelius. Struck with the perusal of the works of Richter, he commenced in 1807 an investigation into the laws of definite proportion. Since that period his labours in this important field have been incessant, and every department of the science has been enriched by his skill and indefatigable industry. Whether we look to pneumatic chemistry, to the chemical history of the metals and of the salts, or to the composition of minerals, we are alike indebted to Berzelius. In all has he traced the laws of definite proportion, and, by a multitude of exact analyses, given to the laws of combination that certainty which accumulated facts can alone convey.

The utility of being acquainted with these important laws is almost too manifest to require mention. Through their aid, and by remembering the equivalents of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. Thus, by knowing that 6 is the equivalent of carbon and 8 of oxygen, it is easy to recollect the composition of carbonic oxide and carbonic acid; the first consisting of 6 parts of carbon + 8 of oxygen, and the second of 6 carbon + 16 of oxygen. The equivalent of potassium is 39; and potassa, its protoxide, is composed of 39 of potassium + 8 of oxygen. From these few data, we know at once the composition of carbonate and bicarbonate of potassa; the former being composed of 22 parts of carbonic acid + 47 potassa, and the latter of 44 carbonic acid + 47 potassa. This method acts as an artificial memory, the advantage of which, compared with the common practice of stating the composition in 100 parts, will be manifest by inspecting the following quantities, and attempting to recollect them.

	Carbonic Oxide.	Carbonic Acid.
Carbon	42.86	27.27
Oxygen	57.14	72.73

	Carbonate of Potassa.	Bicarbonate of Potassa.
Carbonic acid	31.43	47.83
Potassa	68.57	52.17

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently by a simple mental process. The exact quantities of substances required to produce a given effect may be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of great consequence both in the practice of the chemical arts, and in the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful; and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body be found to contain one equivalent of the combustible with 7.99 of oxygen, it is fair to infer that 8, or one equivalent of oxygen, would have been the result, had the analysis been perfect.

The composition of a substance may sometimes be determined by a calculation, founded on the laws of chemical union, before an analysis of it has been accomplished. When the new alkali lithia was first discovered, chemists did not possess it in sufficient quantity for determining its constitution analytically. But the neutral sulphates of the alkalies and alkaline earths are known to be composed of one equivalent of each constituent, and the oxides to contain one equivalent of oxygen. If it be found, therefore, by analysis, that neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 18 of lithia, it may be inferred, since 40 is one equivalent of the acid, that 18 is the equivalent for lithia; and that this oxide is formed of 8 parts of oxygen and 10 of lithium.

The method of determining equivalent numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple substances which possess an extensive range of affinity. Thus water, a compound of oxygen and hydrogen, is found to contain 8 parts of the former to 1 of the latter; and if it be assumed that water consists of one equivalent of oxygen and one of hydrogen, the relative weights of these equivalents will be as 8 to 1. The chemist then selects for analysis such compounds as he believes to contain one equivalent of each element, in which either oxygen or hydrogen, but not both, is present. Carbonic oxide and hydrosulphuric acid are suited to his purpose: as the former consists of 8 parts of oxygen and 6 of carbon, and the latter of 1 part of hydrogen and 16 of sulphur, the equivalent of carbon is inferred to be 6, and that of sulphur 16. The equivalents of all the other elements may be determined in a similar manner.

In researches on chemical equivalents there are two kinds of difficulty, one involved in the processes for ascertaining the exact composition of compounds, and the other in the selection of the compounds which contain single equivalents. Important general precautions in the experimental part of the subject are the following:—1, to exert scrupulous care about the purity of materials; 2, to select methods which consist of a few simple operations only; 3, to repeat experiments, and with materials prepared at different times; 4, to arrive at the same conclusion by two or more processes independent of each other. In the selection of compounds of single equivalents, there are several circumstances calculated to direct the judgment:—

1. If two substances combine in several proportions, the law of multiples usually affects the electro-negative element of a compound. Thus, in the 5 compounds of nitrogen and oxygen, in which oxygen is the negative element, 14 parts of nitrogen are united with 8, 16, 24, 32, and 40 parts of oxygen; whereas, taking the quantity of oxygen as constant, 8 parts of oxygen are united with 14, 7, 4.66, 3.5, and 2.8 parts of nitrogen, in which the simple ratio of the first series does not exist. This circumstance induces the

chemist always to search among the oxides of the same element for the lowest grade of oxidation, and in most cases to consider it as a compound of single equivalents. In some instances, however, the second degree of oxidation is formed of single equivalents, while the lowest oxide consists of two equivalents of the positive element and one of oxygen. Such compounds are called *dioxides* (page 124) and sometimes *suboxides.*

2. Metallic oxides, distinguished for strong alkalinity or for acting as strong alkaline bases, are always protoxides. Dioxides rarely, if ever, unite definitely with acids, and are remarkable for their ready conversion into protoxides with separation of metal. If the same metal yield several oxides, the protoxide is the strongest base; the highest grade of oxidation is frequently an acid, and the intermediate oxides are in general little distinguished either for alkalinity or acidity. Protoxides usually resist decomposition more obstinately than other oxides.

3. When a metal forms two oxides, the oxygen of which is in the ratio of 1 to 1½, the first is usually the protoxide, and the second a compound of two equivalents of the metal to three of oxygen. The oxides of iron and nickel are examples.

4. If two compounds resemble each other in their modes of combination, it is a strong presumption that their constitution is similar. Alumina and the peroxide of iron are remarkably allied in their chemical relations; and hence it is inferred, since the latter consists of two eq. of iron and three eq. of oxygen, that the former, whose composition would otherwise be very doubtful, is composed of two eq. of aluminium and three eq. of oxygen.

5. Mitscherlich has found, as is more fully stated in the article on crystallization, that certain compounds which resemble each other in composition and in their modes of combining, are likewise disposed in crystallizing to affect the same form. Hence it is a strong presumption that compounds which are analogous both in their crystalline figure and modes of combining, are also similar in their composition. In the oxide and acid of chromium, the oxygen is in the ratio 1 to 2, and hence it was at first supposed that one eq. of chromium was united in the oxide with one eq. and in the acid with two equivalents of oxygen. But the chromates resemble the sulphates in form and modes of combining, and the oxide of chromium bears the same analogy to alumina and peroxide of iron. The inference is that oxide of chromium consists of two eq. of chromium and three eq. of oxygen, and chromic acid of one eq. of chromium and three eq. of oxygen.

6. Another guide in these inquiries is derived from the relation traced by Dulong and Petit between the equivalent of a body and its specific heat. The coincidences pointed out at page 35 are sufficiently numerous to show an interesting relation which is sometimes useful in selecting between doubtful numbers; but the instances of failure are at present too frequent to admit of this principle being used except with much caution.

7. The ready decomposition by galvanism, observed by Mr. Faraday, of compounds which consist of single equivalents, and the resistance to the same agent of many others not so constituted, promises to become an indication of great value in determining equivalent numbers. The facts as yet known respecting it will be found in the section on galvanism.

8. Great light is often thrown on the chemical constitution of a compound by a knowledge of the *volumes* of the substances of which it is composed. This subject, however, will be discussed in an after part of this section.

Since the equivalents merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly observed. Thus, the equivalent of hydrogen may be assumed as 10; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000; or, if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers were faithfully preserved. But such a practice would effectually do away with the advantage above ascribed to the use of equivalents; and it is the object of every one to employ such as are simple, that their relation may be perceived by mere inspection. Dr. Thomson makes oxygen 1, so that hydrogen is eight times less than unity, or 0.125, carbon 0.75, and sulphur 2. Dr. Wollaston, in his scale of chemical equivalents, estimated oxygen at 10; and hence hydrogen is 1.25, carbon 7.5, and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry, and others, selected hydrogen as their unit; and, therefore, the equivalent of oxygen is 8. One of these series may easily be reduced to either of the others by an obvious and simple calculation. The numbers adopted in this work refer to hydrogen as unity, and are given in the subjoined table.

CHEMICAL EQUIVALENTS OF ELEMENTARY SUBSTANCES.

Elements.	Equivalents.	Elements.	Equivalents.	Elements.	Equivalents.
Aluminium	13.7	Gold	199.2	Potassium	39.15
Antimony	64.6	Hydrogen	1	Rhodium	52.2
Arsenic	37.7	Iodine	126.3	Selenium	39.6
Barium	68.7	Iridium	98.8	Silicium	7.5
Bismuth	71	Iron	28	Silver	108
Boron	10.9	Lead	103.6	Sodium	23.3
Bromine	78.4	Lithium	10	Strontium	43.8
Cadmium	55.8	Magnesium	12.7	Sulphur	16.1
Calcium	20.5	Manganese	27.7	Tellurium	32.3
Carbon	6.12	Mercury	202	Thorium	59.6
Cerium	46	Molybdenum	47.7	Tin	57.9
Chlorine	35.42	Nickel	29.5	Titanium	24.3
Chromium	28	Nitrogen	14.15	Tungsten	99.7
Cobalt	29.5	Osmium	99.7	Vanadium	68.5
Columbium	185	Oxygen	8	Uranium	217
Copper	31.6	Palladium	53.3	Yttrium	32.2
Fluorine	18.68	Phosphorus	15.7	Zinc	32.3
Glucinium	17.7	Platinum	98.8	Zirconium	33.7

The preceding table is constructed principally from the published tables of Berzelius, and partly from facts supplied by my own researches. The hypothesis that all equivalent numbers are simple multiples of the equivalent of hydrogen, has been elsewhere shown to be untenable. (Phil. Trans. 1833, Part ii. page 523.) Whenever the experimental quantity is nearly a whole number, the last may for many purposes be used as a sufficient approximation; and, accordingly, for such elements as carbon, sulphur, nitrogen, and potassium, which are often referred to in the way of illustration, I have generally adopted round numbers, as being shorter and more easily remembered than fractions. But on all occasions where exact calculations are concerned, the numbers given in the table should be employed.

The useful instrument, known by the name of the *Scale of Chemical Equivalents*, was originally devised by Dr. Wollaston, and is a table of equivalents, comprehending all those substances which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of equivalents, but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of equivalents, we learn that 87 parts, or one equivalent, of sulphate of potassa contain 40 parts of sulphuric acid and 47 of potassa; but recourse must be had to calculation, when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide until 100 marked upon it is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Dr. Wollaston, for a particular account of which I may refer to the Philosophical Transactions for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety, and scales of this kind have been prepared for sale by Dr. Boswell Reid of Edinburgh. A very complete scale of equivalents has been drawn up by Mr. Prideaux of Plymouth. (Phil. Mag. and Annals, viii. 430.)

ATOMIC THEORY.

The brief sketch which has been given of the laws of combination, will, I trust, serve to set in its true light the importance of that department of chemical science. It is founded, as may have been seen, on experiment alone; and the laws which have been stated are the mere expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it. The error which students of chemistry are apt to commit in supposing that the laws of combination involve something uncertain or hypothetical, may easily be traced to its source. It was impossible to reflect on the regularity and constancy with which bodies obey these laws, without speculating about the cause of that regularity: and, consequently, the facts themselves were no sooner noticed than an attempt was made to explain them. Accordingly, when Dr. Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause, and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Wollaston and Davy, recommended and practised an opposite course, both subjects have been too commonly comprised under the head of *atomic theory;* and hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish those parts which are founded on fact, from those which are conjectural. All such perplexity would have been avoided, and this department of the science have been far better understood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from that of the phenomena which it is intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain ultimate particles or molecules, which by their nature are indivisible, and are hence termed *atoms* (from *α not* and *τεμνειν to cut*). These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest, therefore, gradually declined. The progress of modern chemistry has revived the general attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of bodies than was ever advanced before, and one which I conceive is almost irresistible. We have only in fact to assume with Dalton, that all bodies are composed of ultimate atoms, the weight of which is different in different kinds of matter, and we explain at once the foregoing laws of chemical union; and this mode of reasoning is in the present case almost decisive, because the phenomena do not appear explicable on any other supposition.

According to the atomic theory, every compound is formed of the atoms of its constituents. An atom of A may unite with one, two, three, or more atoms of B. Thus, supposing water to be composed of one atom of hydrogen and one atom of oxygen, binoxide of hydrogen will consist of one atom of hydrogen and two atoms of oxygen. If carbonic oxide is formed of one atom of carbon and one atom of oxygen, carbonic acid will consist of one atom of carbon and two atoms of oxygen.

If, in the compounds of nitrogen and oxygen enumerated at page 137, the first or protoxide consist of one atom of nitrogen and one atom of oxygen, the four others will be regarded as compounds of one atom of nitrogen to two, three, four, and five atoms of oxygen. From these instances it will appear, that the law of multiple proportion is a necessary consequence of the atomic theory. There is also no apparent reason why two or more atoms of one substance may not combine with two, three, four, five, or more atoms of another; but, on the contrary, these arrangements are necessary in explanation of the not unfrequent occurrence of half equivalents, as formerly stated. (Page 137.) Such combinations will also account for the complicated proportion noticed in certain compounds, especially in many of those belonging to the animal and vegetable kingdoms.

In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent. For example, instead of describing water as a compound of one equivalent of oxygen and one equivalent of hydrogen, it is said to consist of one atom of each element. In like manner sulphate of potassa is said to be formed of one atom of sulphuric acid and one atom of potassa; the word in this case denoting as it were a compound atom, that is, the smallest integral particle of the acid or alkali,—a particle which does not admit of being divided, except by the separation of its elementary or constituent atoms. The numbers expressing the proportions in which bodies unite, must likewise indicate, consistently with this view, the relative weights of atoms; and accordingly these numbers are often called *atomic weights*. Thus, as water is composed of 8 parts of oxygen and 1 of hydrogen, it follows, on the supposition of water consisting of one atom of each element, that an atom of oxygen must be eight times as heavy as an atom of hydrogen. If carbonic oxide be formed of an atom of carbon and an atom of oxygen, the relative weight of their atoms is as 6 to 8; and in short the chemical equivalents of all bodies may be considered as expressing the relative weights of their atoms.

The foregoing argument in favour of the atomic constitution of matter becomes much stronger, when we trace the intimate connexion which subsists, among many substances, between their crystalline form and chemical composition. This subject, however, now known under the name of *isomorphism* will be more conveniently discussed under the head of crystallization.

Dalton supposes that the atoms of bodies are spherical; and he has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures.

⊙ Hydrogen. ○ Oxygen.
⦶ Nitrogen. ● Carbon.

BINARY COMPOUNDS.

○⊙ Water.
○● Carbonic oxide.

TERNARY COMPOUNDS.

○⊙○ Binoxide of hydrogen.
○●○ Carbonic acid.
&c. &c. &c.

All substances containing only two atoms he called binary compounds, those composed of three atoms ternary compounds, of four quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined.

It is but justice to the memory of the late Mr. Higgins of Dublin, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "Comparative View of the Phlogistic and Antiphlogistic Theories," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid, a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to two of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Mr. Higgins do not appear to have had the slightest connexion with the subsequent views of Dr. Dalton, who in fact seems to have never seen the work of Higgins till after he had given an account of his own doctrine. The observations of Higgins, though highly creditable to his sagacity, do not affect Dalton's merit as an original observer. They were made, moreover, in so casual a manner, as not only not to have attracted the notice of his contemporaries, but to prove that Higgins himself attached no particular interest to them. Dalton's chief merit consists in having formed a complete theory of chemical union, and in the discovery of an essential and most important part of the doctrine, a merit which is solely and indisputably his; but in which he would have been anticipated by Higgins, had that chemist perceived the importance of his own opinions.

To the student who may desire a more ample account of the doctrine of atoms than the nature and limits of this volume admit of being given here, I may recommend a small work by Dr. Daubeny on the atomic theory, which in other respects will be found well worthy of perusal. The advanced student may also consult Dr. Prout's Bridgewater Treatise, where he will find some novel speculations on the agencies which give rise to chemical union, and on the mode in which the combining molecules are arranged; speculations which may well open a path to important views, though in their present form they will scarcely receive the general assent of chemists.

THEORY OF VOLUMES.

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Dr. Dalton explained his views of the atomic constitution of bodies, a paper appeared in the second volume of the *Memoires d'Arcueil* by M. Gay-Lussac, on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple and definite proportions. In the combined researches of himself and Humboldt, those gentlemen found that water is composed precisely of 100 measures of oxygen gas and 200 measures of hydrogen; and Gay-Lussac, being struck by this peculiarly simple proportion, was induced to examine the combinations of other gases, with the view of ascertaining if any thing similar occurred in other instances.

The first compounds which he examined were those of ammoniacal gas with hydrochloric, carbonic, and fluoboric acid gases. 100 volumes of the alkali were found to combine with precisely 100 volumes of hydrochloric acid gas, and they could be made to unite in no other ratio. With both the other acids, on the contrary, two distinct combinations were possible. These are

100	Fluoboric acid gas, with	100	Ammoniacal gas.
100	do.	200	do.
100	Carbonic acid gas	100	do.
100	do.	200	do.

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus ammonia was found by A. Berthollet to consist of 100 volumes of nitrogen gas and 300 volumes of hydrogen; sulphuric acid contains 100 volumes of sulphurous acid and 50 volumes of oxygen; and carbonic acid is formed by burning a mixture of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances Gay-Lussac established the fact, that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c.; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to gases merely, but to vapours also. For example, hydrosulphuric, sulphurous, and hydriodic acid gases are composed of

600 vol.	Hydrogen gas and	100 vol.	vapour of Sulphur.
600	Oxygen	100	. . Sulphur.
100	Hydrogen	100	. . Iodine.

Another remarkable fact established by Gay-Lussac in the same essay is, that the volumes of compound gases and vapours always bear a very simple ratio to the volumes of their elements. This will appear from the following table, in which all the substances are supposed to be in the gaseous state:—

Volumes of Elements.				Volumes of resulting Compounds.
100 Nitrogen	+	300 Hydrogen	yield	200 Ammonia.
50 Oxygen	+	100 Hydrogen	. . .	100 Water.
50 Oxygen	+	100 Nitrogen	. . .	100 Protoxide of nitrogen.
100 Sulphur	+	600 Hydrogen	. . .	600 Hydrosulphuric acid.
100 Sulphur	+	600 Oxygen	. . .	600 Sulphurous acid.
100 Chlorine	+	100 Hydrogen	. . .	200 Hydrochloric acid.
100 Iodine	+	100 Hydrogen	. . .	200 Hydriodic acid.
100 Bromine	+	100 Hydrogen	. . .	200 Hydrobromic acid.
100 Cyanogen	+	100 Hydrogen	. . .	200 Hydrocyanic acid.
100 Oxygen	+	100 Nitrogen	. . .	200 Binoxide of nitrogen.

The law of multiples (page 137) is equally demonstrable by means of combining volumes as by combining weights. The annexed tabular view will justify this statement:—

Volumes of Elements.				Resulting Compounds.
100 Nitrogen	+	50 Oxygen	yield	Protoxide of nitrogen.
100 do.	+	100 do.	. . .	Binoxide of nitrogen.
100 do.	+	150 do.	. . .	Hyponitrous acid.
100 do.	+	200 do.	. . .	Nitrous acid.
100 do.	+	250 do.	. . .	Nitric acid.
100 Hydrogen	+	50 do.	. . .	Water.
100 do.	+	100 do.	. . .	Binoxide of hydrogen.
100 Carbon vapour	+	50 do.	. . .	Carbonic oxide.
100 do.	+	100 do.	. . .	Carbonic acid.

It thus appears that the laws of combination may equally well be deduced from the volumes as from the weights of the combining substances, and that the composition of gaseous bodies may be expressed as well by measure as weight. In the subjoined table is a comparative view of equivalent weights and volumes, to which are added the respective specific gravities in relation both to air and hydrogen: the facts respecting the vapours are drawn from an important essay lately published by Mitscherlich. (An. de Ch. et de Ph. lv. 5.)

GASES AND VAPOURS.	Specific Gravities.		Chemical Equivalents.	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Hydrogen . . .	0.0689	1.00	100	1.00
Nitrogen . . .	0.9727	14.12	100	14.15
Chlorine . . .	2.4700	35.84	100	35.42
Carbon (hypothetical) .	0.4215	6.12	100	6.12
Iodine	8.7020	126.30	100	126.30
Bromine . . .	5.4017	78.40	100	78.40
Water	0.6201	9.00	100	9.00
Alcohol . . .	1.6009	23.24	100	23.24
Sulphuric ether . .	2.5817	37.48	100	37.48
Light carburetted hydrogen	0.5593	8.12	100	8.12
Olefiant gas . . .	0.9808	14.24	100	14.24
Carbonic oxide . .	0.9727	14.12	100	14.12
Carbonic acid . . .	1.5239	22.12	100	22.12
Protoxide of nitrogen .	1.5239	22.12	100	22.15
Sulphurous acid . .	2.2117	32.10	100	32.10
Sulphuric acid (anhydrous)	2.7629	40.10	100	40.10
Cyanogen . . .	1.8157	26.36	100	26.39
Hydrosulphuric acid .	1.1782	17.10	100	17.10
Binoxide of nitrogen .	1.0375	15.06	200	30.15
Mercury . . .	6.9589	101.00	200	202.00
Ammonia . . .	0.5897	8.56	200	17.15
Hydrochloric acid .	1.2694	18.42	200	36.42
Hydriodic acid . .	4.3854	63.65	200	127.30
Hydrobromic acid .	2.7353	39.70	200	79.40
Hydrocyanic acid . .	0.9423	13.68	200	27.39
Arseniuretted hydrogen	2.7008	39.20	200	78.40
Sesquichloride of arsenic .	6.3025	91.46	200	181.66
Sesquiodide of arsenic .	15.6505	227.15	200	454.30
Protochloride of mercury .	8.1939	118.92	200	237.42
Bichloride of mercury .	9.4289	136.84	200	272.84
Bromide of mercury .	9.6597	140.20	200	280.40
Bibromide of mercury .	12.3606	179.40	200	358.80
Biniodide of mercury .	15.6609	227.30	200	454.60
Oxygen . . .	1.1024	16.00	50	8.00
Arsenious acid . .	13.6972	198.80	50	99.40
Phosphorus . . .	4.3269	62.80	25	15.70
Arsenic	10.3901	150.80	25	37.70
Sulphur . . .	6.6558	96.60	16.66	16.10
Bisulphuret of mercury. .	5.3788	78.06	300	234.20

The observations which more immediately flow from the facts in the preceding table are these:—

1. The combining volumes of substances, both elementary and compound, are either equal, or have the simple ratio of 1 to 2, 1 to 3, &c. The same simplicity rarely exists among the equivalent weights.

2. On comparing together the third and fifth columns, the corresponding

numbers for the 18 first substances will be found nearly or quite identical. As *those* substances have the same uniting volume as hydrogen, which is the assumed unit of comparison, and as the specific gravities are merely the weights of equal volumes, the numbers of the third column, were they quite exact, must coincide with those in the fifth: their want of identity indicates errors of observation.

3. The identity in the equivalent volumes of the elementary gases, hydrogen, nitrogen, and chlorine, led to the notion that the equivalent volumes of most other elements, such as carbon, sulphur, and phosphorus, might also be identical. *Assuming* that identity, the specific gravity which those elements ought to have when gaseous, may easily be calculated. Thus, taking 1, 6.12, and 16.1 as the equivalents of hydrogen, carbon, and sulphur, then will their specific gravities in the gaseous state, combining volumes being supposed equal, be in the ratio of 1, 6.12, and 16.1. This method, by which the hypothetical specific gravity of carbon, as stated in the table, was obtained, was first indicated by Dr. Prout. (An. of Phil. vi. 321.) But though such hypothetical numbers may sometimes be used for the convenience of expressing the relation of uniting substances by measure, recent facts show how dangerous it would be to confide in them; for by the table it appears that the equivalent volume of sulphur vapour is one-sixth of that of hydrogen, which renders the specific gravity of the vapour of sulphur six times greater than the hypothetical number. Similar deviation is observable in phosphorus, arsenic, and mercury. In these cases, the real specific gravity of a vapour is as much greater than the hypothetical, as its equivalent volume is less than that of hydrogen.

4. The identity in the equivalent volumes of hydrogen, nitrogen, and chlorine, suggested the idea that the atoms or indivisible molecules of all the elements are of the same magnitude; and this coupled with the supposition that the self-repulsive energy of these atoms is equal, led to the opinion that equal volumes of the elements in the gaseous state must contain an equal number of atoms. This hypothesis, recommended by its simplicity, and supported by the fact that the volumes of gaseous substances vary according to the same law by varying temperature and pressure, was accordingly employed as a mode of determining the relative weights of atoms. As water consists of 50 measures of oxygen and 100 of hydrogen gas, it was inferred to be a compound of one atom of oxygen and two atoms of hydrogen; and consequently, taking 8 as the weight of an atom of oxygen, the weight of one atom of hydrogen is ½ instead of 1, as in the table; or taking hydrogen as 1, the atom of oxygen is 16. On the same principle may the numbers which in the table represent the equivalent weights of chlorine, bromine, iodine, and nitrogen, which have the same equivalent volumes as hydrogen, be considered as the weights of two equivalents. The equivalents adopted by Davy in his Elements of Chemical Philosophy, as well as those of Berzelius, which are now in general use on the Continent, were framed in accordance with these views: this the British chemist requires to bear in mind, since the same numbers which Berzelius uses for 2 equivalents of hydrogen, nitrogen, chlorine, bromine, and iodine, he considers as one equivalent. But the opinion of Davy and Berzelius must now either be abandoned, or maintained on other principles; since the late researches of Dumas and Mitscherlich have shown experimentally that equal volumes of the elementary gases and vapours do not contain the same number of atoms.

5. The facts contained in the last and preceding tables supply materials for calculating the sp. gravity of compound gases, by which means the accuracy of other conclusions respecting their composition may be verified. Thus analysis proves that ammoniacal gas is composed of 100 volumes of nitrogen, and 300 of hydrogen gases, condensed into the space of 200 volumes: if so, its sp. gravity will be

$$\frac{0.9727+3\times 0.0689}{2}=\frac{1.1794}{2}=0.5897,$$

The near agreement of this calculated number with that found by weighing the gas itself, proves that ammonia has really the constitution above assigned to it, and gives great probability that the sp. gravity of nitrogen and hydrogen gases is nearly correct.

Again, hydrochloric acid gas consists of 100 volumes of hydrogen and 100 of chlorine gases, united without any change of bulk. Hence its sp. gravity ought to be

$$\frac{2.47+0.0689}{2}=1.2694$$

Hydrocyanic acid vapour is formed of 100 volumes of hydrogen and 100 of cyanogen gases united without change of volume; and, therefore, its sp. gravity should be

$$\frac{1.8157+0.0689}{2}=0.9423.$$

Considering olefiant gas as a compound of 200 volumes of hydrogen gas and 200 of the vapour of carbon condensed into 100, its sp. gravity will be $2\times0.0689+2\times0.4215=0.1378+0.8430=0.9808$.

Aqueous vapour is composed of 100 volumes of hydrogen and 50 of oxygen gases condensed into the space of 100 volumes; and, therefore, its sp. gravity ought to be $0.0689+0.5512$ (half the sp. gr. of oxygen) $=0.6201$.

Protoxide of nitrogen is formed of 100 volumes of nitrogen and 50 of oxygen gases condensed into 100 volumes, and hence its sp. gravity should be $0.9727+0.5512=1.5239$.

Assuming carbonic oxide to be a compound of 100 volumes of carbon vapour and 50 of oxygen gas contracted in uniting into 100 volumes, its sp. gravity should be $0.4215+0.5512=0.9727$.

As the different sp. gravities thus calculated are very nearly those found by direct experiment, there is a strong presumption that the elements of the calculations are correct.

The principle of these calculations is sufficiently obvious. The sp. gravities represent the weights of equal volumes of the gases: taking 100 as the standard volume of which the sp. gravity of each gas denotes the weight, then 50 volumes of a gas may be indicated by half, 25 volumes by a fourth, and 16.66 by a sixth of its specific gravity. Thus hydrosulphuric acid is a compound of 100 volumes of hydrogen gas, and 16.66 $(\frac{100}{6})$ of the vapour of sulphur, condensed into 100 volumes, and, therefore, its sp. gravity is

$$0.0689+\frac{6.6558}{6}=0.0689+1.1093=1.1782.$$

Sulphurous acid consists of 100 volumes of oxygen gas and 16.66 of the vapour of sulphur condensed into 100 volumes; and hence its sp. gravity is

$$1.1024+\frac{6.6558}{6}\quad 1.1024+1.1093=2.2117.$$

In these two gases the volume is the same as the hydrogen or oxygen which they contain, and, therefore, their sp. gravities are the sum of the sp. gravities of their elements. The same applies to water, protoxide of nitrogen, and carbonic oxide. In olefiant gas 400 volumes are condensed into 100, and, therefore, its sp. gravity is the sum of the sp. gravities of its elements. Hydrochloric acid gas occupies the same space as its elements, and, therefore, its sp. gravity is found by taking the mean of their sp. gravities. The same remark applies to hydrocyanic acid. In ammonia 400 volumes are condensed into 200, and, therefore, the sum of the sp. gravities is halved.*

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* The statements in this paragraph are rather loosely expressed. We may, as Dr. Turner remarks in a preceding paragraph, assume the specific gravity

As vapours are easily condensed by cold, and in many cases exist as such only at high temperatures, their sp. gravities may often be obtained by calculation more accurately than by experiment. Thus it is easier accurately to ascertain the sp. gravity of hydrogen and hydrosulphuric acid gases than of the vapour of sulphur; and, therefore, as soon as experiment has shown that the sp. gravity of that vapour is *somewhere about* 6.6558, then the precise number may be calculated. For as 100 volumes of hydrosulphuric acid gas contain 100 of hydrogen gas, the sp. gravity of the latter deducted from that of the former (1.1782—0.0689,) gives 1.1093 as the weight of combined sulphur. If the equivalent volume of sulphur were 100, then must 1.1093 be its sp. gravity; but as the number found experimentally is nearly six times 1.1093, the inference is that the real sp. gravity is 6×1.1093=6.6558, and that its equivalent volume is six times less than 100, or 16·66. The only assumption here is, that if the equivalent volume of the vapour is not 100, it must be some multiple or submultiple of it by a whole number, consistently

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of the different gases to be the weight of some standard volume of each of them, as for example 100 volumes; and, on this assumption, it will follow that on ascertaining the weight of 100 volumes of any gas, we shall have its specific gravity. The general formula applicable to these calculations, therefore, is to deduce from the known specific gravities of certain gases, from the proportion in which they unite in volume, and from the resulting volume, the weight of 100 volumes of the compound gas which may be formed; for if the known sp. gr. in all cases be assumed to represent the weight of 100 volumes, reciprocally the weight of 100 volumes, when ascertained, will represent the sp. gr. In ascertaining then the weight of 100 volumes of a compound gas, the first step is to add together the weights of the known volumes of its constituents; these weights being deduced from the assumption that the weight of every 100 volumes of each constituent is represented by its specific gravity. The sum thus obtained will be the weight of the resulting volume, and, if this happen to be 100 volumes, the answer is furnished at once. But if the resulting volume should not be 100 volumes, then, by the rule of proportion, the weight of 100 volumes of the compound gas is to be ascertained thus: if the known number of volumes in the resulting volume weigh the sum obtained as above mentioned, what will 100 volumes weigh? The weight of 100 volumes thus ascertained necessarily represents the specific gravity. The simplest case under the rule is when 100 volumes, respectively, of the constituents of a compound gas are condensed into 100 volumes; for here the sp. gravities of the constituent gases represent at once the entire volume of each constituent entering into combination; and their sum gives the sp. gr. of the compound; because it represents the weight of 100 volumes. An instance of this simplest case is afforded by carbonic acid, in which 100 volumes of carbon vapour and 100 volumes of oxygen are condensed into 100 volumes. Here it is only necessary to add together 0.4215 (sp. gr. of carb. vap.) and 1.1024 (sp. gr. of oxygen,) and the sum, 1.5239, is the sp. gr. of carbonic acid. It is only in this simplest case that the sp. gr. of a compound gas is the sum of the sp. gravities of its constituents. Dr. Turner is inaccurate, therefore, when he states that hydrosulphuric and sulphurous acid gases furnish cases in which their sp. gravities are the sum of the sp. gravities of their elements: for though, in the instances of these two gases, the sp. gravities of the hydrogen and oxygen may be taken, since these elements are present in the amount of 100 volumes; yet the sp. gr. of the sulphur vapour cannot be taken, as it is not the weight of 100 volumes of this vapour which is required, but the weight of one-sixth of 100 volumes. Dr. Turner's inaccuracy consists in this, that he calls the weight of the given number of volumes of each constituent gas, its sp. gr.; whereas such weight is to be assumed to be the sp. gr., only in case it is the weight of 100 volumes. Thus, in the case of olefiant gas, cited by Dr. Turner, its sp. gr. is not the sum of the sp. gravities of its elements, but the sum of double the sp. gr. of its elements.—*Ed.*

with the *theory of volumes*. In the construction of the preceding table I have given the sp. gravities of vapours calculated on these principles rather han the precise numbers given by experiment.

CHEMICAL SYMBOLS.

The impracticability in many cases of contriving convenient names expressive of the constitution of chemical compounds, especially of minerals, suggested the employment of symbols as an abbreviated mode of denoting the composition of bodies. It was thought that the names of elementary substances, instead of being written at full length, might often be more conveniently indicated by the first letter of their names; and that the combination of elements with each other might be expressed by placing together, in some way to be agreed on, the letters which represent them. The advantage of such a symbolic language was felt so strongly by Berzelius, that he some years ago contrived a set of symbols, which he has since used extensively in his writings; and other eminent chemists as well as mineralogists, believing symbols to be useful, adopted those which Berzelius had proposed. The consequence is, that symbolic expressions, called *chemical formulæ*, are now so much resorted to, and are so identified with the language of chemistry, that essays of great value are in a measure as sealed books to those who cannot read symbols. It is, therefore, important that the chemical student, whatever he may think of the value of symbols, should not be unacquainted with them. Fortunately, the labour of a few minutes will enable him to understand the subject. The following table includes the symbols of all the elementary substances according to Berzelius.

TABLE OF SYMBOLS.

Elements	Symb.	Elements.	Symb.	Elements.	Symb.
Aluminium	Al	Gold (Aurum)	Au	Potassium(Kalium)	K
Antimony(Stibium)	Sb	Hydrogen	H	Rhodium	R
Arsenic	As	Iodine	I	Selenium	Se
Barium,	Ba	Iridium	Ir	Silicium	Si
Bismuth	Bi	Iron (ferrum)	Fe	Silver (Argentum)	Ag
Boron	B	Lead Plumbum)	Pb	Sodium (Natrium)	Na
Bromine	Br	Lithium	L	Strontium	Sr
Cadmium	Cd	Magnesium	Mg	Sulphur	S
Calcium	Ca	Manganese	Mn	Tellurium	Te
Carbon	C	Mercury (Hydrargyrum)	Hg	Thorium	Th
Cerium	Ce	Molybdenum	Mo	Tin (Stannum)	Sn
Chlorine	Cl	Nickel	Ni	Titanium	Ti
Chromium	Cr	Nitrogen	N	Tungsten (Wolfram)	W
Cobalt	Co	Osmium	Os	Vanadium	V
Columbium (Tantalum)	Ta	Oxygen	O	Uranium	U
Copper (Cuprum)	Cu	Palladium	Pd	Yttrium	Y
Fluorine	F	Phosphorus	P	Zinc	Zn
Glucinium	G	Platinum	Pl	Zirconium	Zr.

For the sake of uniformity, and to prevent confusion, it is much to be wished that these symbols, being now generally known, should be rigorously adhered to. Berzelius has properly selected them from Latin names, as being known to all civilized nations; and when the names of two or more elements begin with the same letter, the distinction is made by means of an additional letter.

The foregoing symbols are intended to represent the chemical equivalents of the elements. Thus, the letters H, I, and Ba, stand for one equivalent of hydrogen, iodine, and barium; and 2H, 3H, and 4H, for 2, 3, and 4 equivalents of hydrogen. Two equivalents of an element are often denoted by placing a dash through or under its symbol: for instance, $\cancel{\mathrm{H}}$ or $\underline{\mathrm{H}}$ means 2H, and $\cancel{\mathrm{P}}$ or $\underline{\mathrm{P}}$ signifies 2P. Certain compounds are often, for the sake of brevity, denoted by single symbols in the same manner as the elements; thus an equivalent of water, ammonia, and cyanogen, is sometimes expressed by Aq, Am, and Cy; but in general the formulæ for compound bodies are so contrived as to indicate the elements they contain, and the mode in which they are united. This may be done in several ways; but that which first suggests itself, is to connect together the symbols by the same signs as are used in Algebra. Thus the formulæ $\mathrm{K+O}$, $\mathrm{Ca+O}$, $\mathrm{Ba+O}$, $\mathrm{Mn+O}$, $\mathrm{Fe+O}$, $\mathrm{2Fe+3O}$, $\mathrm{3H+N}$, $\mathrm{2H+2C}$, $\mathrm{C+2O}$, $\mathrm{N+5O}$, $\mathrm{S+3O}$, and $\mathrm{H+Cl}$, denote single equivalents of potassa, lime, baryta, protoxide of manganese, protoxide of iron, peroxide of iron, ammonia, olefiant gas, carbonic acid, nitric acid, sulphuric acid, and hydrochloric acid. The formula $\mathrm{K+N+6O}$ indicates the elements which are contained in an equivalent of nitrate of potassa: in order to express further that the potassium is combined with only one equivalent of oxygen, the remaining oxygen with the nitrogen, and the potassa with nitric acid, the symbols are placed thus,—$\mathrm{(K+O)+(N+5O)}$, the brackets containing the symbols of those elements which are supposed to be united. A number placed on the outside of a bracket multiplies the compound within it: thus $\mathrm{(K+O)+(S+3O)}$ is sulphate of potassa, and $\mathrm{(K+O)+2(S+3O)}$ is the bisulphate. All the elements contained in a compound are thus visibly represented, and the chemist is able readily to trace all possible modes of combination, and to select that which is most in harmony with the facts and principles of his science. He may, and often does, thereby detect relations which might otherwise have escaped notice.

Another advantage attributable to such formulæ is, that they facilitate the comprehension of chemical changes. If hydrosulphuric acid acts upon the protoxide of lead, it is easy to say that the sulphur combines with the lead and the hydrogen with the oxygen; but the exact adaptation of the quantities for mutual interchange appears to me more clearly shown by symbols than by a description or a diagram, both of which are apt to produce confusion where the change to be explained is complex. In the simple instance alluded to, $\mathrm{H+S}$ reacts on $\mathrm{Pb+O}$, and the products are $\mathrm{Pb+S}$ and $\mathrm{H+O}$. When hydrosulphuric acid acts on bicyanuret of mercury, the result is bisulphuret of mercury and hydrocyanic acid: the substances which interchange elements are $\mathrm{2(H+S)}$ and $\mathrm{Hg+2Cy}$; and the products are $\mathrm{Hg+2S}$, and $\mathrm{2(H+Cy.)}$ In more complicated changes the advantage of chemical formulæ is still more manifest, examples of which kind will be found in the section on cyanogen, and in other parts of this volume.

Useful as the algebraic chemical formulæ are for the purpose of studying chemical changes, they are sometimes found inconveniently long where the object is merely to express the composition of bodies, and accordingly Berzelius has introduced several abbreviations. For instance, he indicates degrees of oxidation by dots placed over the symbol, writing $\dot{\mathrm{K}}$, $\ddot{\mathrm{C}}$, $\overset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{N}}}$, instead of $\mathrm{K+O}$, $\mathrm{C+2O}$, $\mathrm{N+5O}$, for potassa, carbonic acid, and nitric acid. In like manner he denotes compounds of sulphur by commas, writing $\overset{,}{\mathrm{K}}$, $\overset{,,}{\mathrm{Hg}}$, $\overset{,}{\mathrm{H}}$ instead of $\mathrm{K+S}$, $\mathrm{Hg+2S}$, $\mathrm{H+S}$, for sulphuret of potassium, bisulphuret of mercury, and hydrosulphuric acid. When the ratio is that of 2 to 3 he employs the symbol for two equivalents above stated; thus, $\underline{\overset{\cdot\cdot\cdot}{\mathrm{Fe}}}$, $\underline{\overset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{P}}}}$, $\underline{\overset{\cdot\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{As}}}}$ is used instead of $\mathrm{2Fe+3O}$, $\mathrm{2P+5O}$, $\mathrm{2As+5O}$, for an equivalent of peroxide of iron, phosphoric acid, and arsenic acid; and similarly we have $\underline{\overset{\prime\prime\prime}{\mathrm{As}}}$, $\underline{\overset{\prime\prime}{\overset{\prime\prime\prime}{\mathrm{As}}}}$ instead of $2As+3S$, $2As+5S$ for the sesquisulphuret and persulphuret of arsenic. These last formulæ are sometimes used to indicate two equivalents instead of one, as was done in the last edition of these elements; but as, agreeably to the atomic theory, the smallest possible molecule of peroxide of iron consists of 2 atoms of iron and 3 of oxygen, the formula $2Fe+3O$ ought to stand for one equivalent only.

Berzelius often dispenses with the sign $+$, and writes combined elements side by side, the sign of addition being understood instead of expressed. Thus he uses $\dot{\mathrm{K}}\dddot{\mathrm{S}}$, $\dot{\mathrm{Ca}}\ddot{\mathrm{C}}$, $\dot{\mathrm{Ba}}\overset{\cdot\cdot}{\dddot{\mathrm{N}}}$, $\dot{\mathrm{K}}\dddot{\mathrm{S}}+\dot{\mathrm{Ni}}\dddot{\mathrm{S}}$, instead of $\dot{\mathrm{K}}+\dddot{\mathrm{S}}$, $\dot{\mathrm{Ca}}+\ddot{\mathrm{C}}$, $\dot{\mathrm{Ba}}+\overset{\cdot\cdot}{\dddot{\mathrm{N}}}$, $(\dot{\mathrm{K}}+\dddot{\mathrm{S}})+(\dot{\mathrm{Ni}}+\dddot{\mathrm{S}})$, for sulphate of potassa, carbonate of lime, nitrate of baryta, and the double sulphate of potassa and oxide of nickel. Two or more equivalents of one constituent of a compound are denoted by numbers placed in the same position as the indices of powers in algebra: thus NH^3, NC^2, $\underline{\dddot{\mathrm{Fe}}}^2\dot{\mathrm{H}}^3$ is the abbreviation of $N+3H$, $N+2C$, $2\underline{\dddot{\mathrm{Fe}}}+3\dot{\mathrm{H}}$, for ammonia, cyanogen, and sesquihydrate of iron, a compound of 2 equivalents of peroxide of iron and 3 of water. A number used before symbols, like coefficients in algebra, multiplies all the following symbols not separated from it by a $+$ sign. Thus in $8\dot{\mathrm{Ca}}\dot{\mathrm{Si}}^3+\dot{\mathrm{K}}\dot{\mathrm{Si}}^6+16\,\mathrm{Aq}$ (which is the formula for the mineral called apophyllite), the 8 denotes 8 equivalents of $\dot{\mathrm{Ca}}\dot{\mathrm{Si}}^3$, or tersilicate of lime, which are united with 1 equivalent of sexsilicate of potassa, and 16 of water.

Berzelius also expresses the vegetable and animal acids by the first letter of their name, with a dash over it. Thus $\overline{\mathrm{T}}$, $\overline{\mathrm{A}}$, $\overline{\mathrm{C}}$, $\overline{\mathrm{B}}$, $\overline{\mathrm{G}}$, $\overline{\mathrm{F}}$, are the symbols for tartaric, acetic citric, benzoic, gallic, and formic acids.

ISOMERIC BODIES.

It was formerly thought that the same elements united in the same ratio must always give rise to the same compound; but within these few years several examples have been discovered of two or more substances containing the same elements in the same ratio, and yet exhibiting chemical properties distinct from each other. For such compounds Berzelius has suggested the general appellation of *isomeric*, from *ισος equal* and *μερος part*, expressive of equality in the ingredients. Interesting instances of this kind are the two cyanic acids, which consist of cyanogen and oxygen in the same ratio, and have the same equivalent, yet differ widely in their chemical properties; and a similar example is afforded by the tartartic and paratartaric acids. Berzelius proposed to prefix *para* in this instance, from *παρα near to*, as indicative of the close alliance between the two compounds, a principle of nomenclature which will probably be found applicable on other occasions.

Unexpected as was the discovery of isomerism, it is quite consistent with our theories of chemical union; insomuch as the same elements may be grouped or combined in different ways, and thereby give rise to compounds essentially distinct. Thus the elements of sulphate of potassa may perhaps be united indiscriminately with each other, as expressed by the formula KSO^4; or they may form $KO+SO^3$; or $KS+O^4$; or KO^2+SO^2; and other combinations might be made. The second of these is doubtless the real one; but no one can say that the others are impracticable. Again, the elements of peroxide of tin, Sn and 2O, may either form SnO^2, or $SnO+O$; and those of the peroxide of iron, 2Fe and 3O, may either be Fe^2O^3, or $FeO+FeO^2$, not to mention other possible combinations. The elements of alcohol are 2C, 3H, and O, which may be united indiscriminately as H^3C^2O, or H^3C^2+O, or as H^2C^2+HO, besides others: it is commonly considered a compound of olefiant gas and water, as indicated by the last formula.

Some bodies consist of the same elements in the same ratio, and yet differ in their equivalents. A marked example is supplied by olefiant gas and etherine, the former of which contains 200 volumes of carbon vapour and 200 of hydrogen gas condensed into 100 volumes, and the latter, 400 volumes of carbon vapour and 400 of hydrogen gas, united so as to yield 100 volumes of etherine. The equivalent of olefiant gas is 14.24, and that of etherine 28.48, or exactly double. A similar case will be found in the description of cyanuric acid. The nature of these compounds is at once detected by their equivalents being unlike, and by the volume which they occupy as gases compared with the volumes of the elements of which they consist. Isomeric bodies of this kind are obviously much less intimately allied than those above described.

SECTION III.

OXYGEN.

Oxygen gas was discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. Several appellations have been given to it. Priestley named it *dephlogisticated air*; it was called *empyreal air* by Scheele, and *vital air* by Condorcet. The name it now bears, derived from the Greek words οξυς *acid* and γενναω *to generate*, was proposed by Lavoisier, who considered it the sole cause of acidity.

Oxygen gas may be obtained from several sources. The peroxides of manganese, lead, and mercury, nitre, and chlorate of potassa, yield it in large quantities when they are exposed to a red heat. The substances commonly employed for the purpose are peroxide of manganese and chlorate of potassa. It may be procured from the former in two ways; either by heating it to redness in a gun-barrel, or in a retort of iron or earthenware; or by putting it in fine powder into a flask with about an equal weight of concentrated sulphuric acid, and heating the mixture by means of a lamp. To understand the theory of these processes, it is necessary to bear in mind the composition of the three following oxides of manganese:—

	Manganese.	Oxygen.	
Protoxide .	27.7 or 1 equiv.	+ 8 .	=35.7
Sesquioxide .	27.7 .	+ 12 .	=39.7
Peroxide .	27.7 .	+ 16 .	=43.7

On applying a red heat to the last, it parts with half an equivalent of oxygen, and is converted into the sesquioxide. Every 43.7 grains of the peroxide will, therefore, lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about 128 cubic inches of gas. The action of sulphuric acid is different. The peroxide loses a whole equivalent of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 43.7 grains of peroxide must consequently yield 8 grains of oxygen and 35.7 of protoxide, which by uniting with one equivalent (40) of the acid, forms 75.7 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from peroxide of manganese, though hardly ever quite pure, owing to the presence of iron, carbonate of lime, and other earthy substances, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from carbonate of lime by dilute hydrochloric or nitric acid; but when oxygen of great purity is required, it is better to obtain it from chlorate of potassa. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free from water, and then, on increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called chloride of potassium, which is left in the retort. The composition of the chloric acid and potassa which constitute the salt, is stated below;—

Chlorine .	35.42 or 1 eq.	Potassium .	39.15 or 1 eq.
Oxygen .	40 or 5 eq.	Oxygen .	8 or 1 eq.
Chloric acid	75.42 or 1 eq.	Potassa .	47.15 or 1 eq.

Hence the oxygen which passes over from the retort, is derived partly from the potassa and partly from the chloric acid; while chlorine and potassium enter into combination. Thus are 122.57 grains of the chlorate resolved into 74.57 grains of chloride of potassium, and 48 grains, or about 161 cubic inches, of pure oxygen.

Oxygen gas is colourless, has neither taste nor smell, is not chemically affected by the imponderables, refracts light very feebly, and is a non-conductor of electricity. It is the most perfect negative electric that we possess, always appearing at the positive pole when any compound which contains it is exposed to the action of galvanism.. It emits light, as well as heat, when suddenly and forcibly compressed; but Thenard has shown that the light is entirely owing to the combustion of the oil with which the compressing tube is lubricated. When not united with other ponderable matter, it is always in the form of gas; but even in this its purest state it is probably combined, as is most likely true of all elementary principles, with heat, light, and electricity.

Oxygen gas is heavier than atmospheric air. The principal estimates vary from 1.1026, that of Dulong and Berzelius, to 1.1111 as given by Dr. Thomson. Judging from the care devoted to the inquiry, the observation of Dulong and Berzelius appears to me most deserving of confidence, and I have accordingly adopted 1.1026 as correct; but it is so important to know the exact specific gravity of oxygen gas, that chemists anxiously look for the result of the observations which Dr. Prout is understood to have been long engaged in on this subject. Adopting 1.1024, the number given in the table, page 146, 100 cubic inches, when the thermometer is at 60° F. and the barometer stands at 30 inches, would weigh 34.1872 grains.

Oxygen gas is very sparingly absorbed by water, 100 cubic inches of that liquid dissolving only three or four of the gas. It has neither acid nor alkaline properties; for it does not change the colour of blue flowers, nor does it evince a disposition to unite directly either with acids or alkalies. It has a very powerful attraction for most simple substances; and there is not one of them with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and bodies which have united with it are said to be *oxidized*. The compounds so formed are divided by chemists into acids and oxides. The former division includes those compounds which possess the general properties of acids; and the latter comprehends those which not only want that character, but of which many are highly alkaline, and yield salts by uniting with acids. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation; and all inflammable or combustible substances derive their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as is exemplified by the rusting of iron when exposed to a moist atmosphere. Different as these processes may appear, oxidation is the result of both; and both depend on the same circumstance, namely, the presence of oxygen in the atmosphere.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen gas. A piece of wood, on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the imflammables, undergo rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be closed, the light will in a short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished. This result is general. The burning of one body in a given portion of oxygen unfits it more or less completely for supporting the combustion of another; and the reason is manifest. Combustion is produced by the combination of inflammable matter with oxygen. The quantity of free oxygen, therefore, diminishes during the process, and is at length nearly or quite exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. The oxygen often loses its gaseous form as well as its other properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen gas suffers diminution of volume only, or it may even undergo no change of bulk at all, as is exemplified by the combustion of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is then an oxidized body, and cannot be made to burn even by aid of the purest oxygen gas. It has also increased in weight. It is an error to suppose that bodies lose any thing while they burn. The materials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the required care, the combustible matter is always found to weigh more after than before combustion; and the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen gas is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if put into a portion of air from which the oxygen has been previously removed by a burning body. It may, therefore, be anticipated that oxygen is consumed during respiration. If a bird be confined in a limited quantity of atmospheric air, it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have, therefore, the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor, in general, can a candle burn in air which contains too little oxygen for respiration.

It is singular that, though oxygen is necessary to respiration, in a state of purity it is deleterious. When an animal, as a rabbit for example, is supplied with an atmosphere of pure oxygen gas, no inconvenience is at first perceived; but after the interval of an hour or more, the circulation and respiration become very rapid, and the system in general is highly excited. Symptoms of debility subsequently ensue, followed by insensibility; a death occurs in six, ten, or twelve hours. On examination after death, the blood is found highly florid in every part of the body, and the heart acts strongly even after the breathing has ceased. For these experiments we are indebted to Mr. Broughton.

THEORY OF COMBUSTION.

The only phenomena of combustion noticed by an ordinary observer, are the destruction of the burning body, and the developement of heat and light; but it has been demonstrated that in addition to these circumstances, oxygen gas invariably disappears, and a new compound consisting of oxygen and the combustible is generated. The term *combustion*, therefore, in its common signification, implies the rapid union of oxygen gas and combustible matter, accompanied with heat and light. As the evolution of heat and light is dependent on chemical action, the same phenomena may be expected in other chemical processes; and, accordingly, heat and light are frequently emitted quite independently of oxygen. Thus phosphorus takes fire, and a taper burns for a short time, in a vessel of chlorine; and several of the common metals, such as copper, antimony, and arsenic, in a state of fine division, become red-hot when introduced into a jar of that gas. Potassium takes fire in cyanogen gas; and copper-leaf or iron wire, if moderately heated, undergoes the same change in the vapour of sulphur. A mixture of iron filings and sulphur, when heated so as to bring the latter into perfect fusion, emits intense heat and light at the instant of combination; and a like effect, though in a far less degree, is produced by the action of concentrated sulphuric acid on pure magnesia. Most of these and similar examples, especially when one of the combining substances is gaseous, are frequently included under the idea of combustion; and they certainly belong to the same class of phenomena. In the subsequent observations, however, I shall employ the term in its ordinary sense; but the remarks concerning increase of temperature, whether with or without light, apply equally to all cases where heat is developed as a result of chemical action.

For many years prior to the discovery of oxygen gas, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when the body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated,—that combustion and oxidation in general consist in the combination of combustible matter with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared, that the phosphorus gained materially in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to that which had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Dr. Black's theory of latent heat. Heat is always evolved, whenever a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies; because a quantity of heat previously combined, or latent, within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid; and in forming phosphoric acid with phosphorus, or in oxidizing metals, oxygen is condensed into a solid. When the product of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a smaller quantity of combined heat, or has a smaller specific heat, than the substances by which it is produced.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by increase of temperature, and the heat evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When combustion, or any other chemical action, is followed by considerable condensation, in consequence of which the new body contains less insensible heat than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this were the sole cause of the phenomenon, a rise of temperature should always be preceded by a corresponding diminution of specific heat, and the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject, (Annales de Chim. et de Phys. vol. x.) that the degree of heat developed during combination, bears no relation to the specific heat of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the specific heat of the compound. It is a well known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible heat than the substances from which they were formed. This happens remarkably in the explosion of gunpowder, which is attended by intense heat; and yet its materials, in passing from the solid to the gaseous state, expand to at least 250 times their volume, and consequently render latent a large quantity of heat.

These circumstances leave no doubt that the evolution of heat during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that part of the effect must be owing to it on those occasions, when the phenomena appear to depend on change of specific heat alone. A new theory is, therefore, required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to increase of temperature. Berzelius, in adopting the electro-chemical theory, regards the heat of combination as an electrical phenomenon, believing it to arise from the oppositely electrical substances neutralizing one another, in the same manner as the electric equilibrium is restored during the discharge of a Leyden jar. There are indeed strong grounds for believing that electrical action is an essential part of every chemical change, and it is probable that the heat developed during the latter may be due to the former; but this part of science is as yet too imperfect for indicating the precise mode by which the effect is produced.

The heat emitted during combustion varies with the nature of the material. The effect of the combustible gases in raising the temperature of water, according to the experiments of Dr. Dalton, is shown in the following table.—(Chemical Philosophy, ii. 309.)

Hydrogen, in burning, raises an equal volume of water .	5° F.
Carbonic oxide	4½
Light carburetted hydrogen	18
Olefiant gas	27
Coal gas varies with the quality of the gas from . .	10 to 16
Oil gas varies also with the quality of the gas from .	12 to 20

Dr. Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

In the thirty-seventh volume of the An. de Ch. et de Ph., page 180, M. Despretz has given a notice of some experiments on the heat developed in combustion. The substances burned were hydrogen, carbon, phosphorus, and several metals; and so much of each was employed, as to require the same quantity of oxygen. When the combustion of hydrogen gas produced 2578 degrees of heat, carbon gave out 2967, and iron 5325. Phosphorus, zinc, and tin emit quantities of heat very nearly the same as iron. Hence it follows that, for equal quantities of oxygen, hydrogen in burning evolves less heat than most other substances. These results do not accord with those of Dalton.

SECTION IV.

HYDROGEN.

This gas was formerly termed *inflammable air*, from its combustibility, and *phlogiston*, from the supposition that it was the matter of heat; but the name *hydrogen*, from *ὕδωρ water*, and *γεννειν* to *generate*, has now become general. Its nature and leading properties were first pointed out in the year 1766 by Mr. Cavendish. (Philos. Trans. lvi. 144.)

Hydrogen gas may be easily procured in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough. The second and most convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid and four or five of water. Zinc is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The gas evolved during the solution of iron has an offensive odour, ascribed by Berzelius to the presence of a volatile oil, which may be almost entirely removed by transmitting the gas through alcohol. The oil appears to arise from some compound being formed between hydrogen, and the carbon which is always contained even in the purest kinds of common iron; and it is probable that a little carburetted hydrogen gas is generated at the same time. The zinc of commerce contains sulphur, and almost always traces of charcoal, in consequence of which it is contaminated with hydrosulphuric acid, and probably with the same impurities, though in a less degree, as are derived from iron. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potassa. To obtain hydrogen of great purity, distilled zinc should be employed.

Hydrogen is a colourless gas, when pure has neither odour nor taste, and is a powerful refractor of light. Like oxygen, it cannot be resolved into more simple parts, and, like that gas, has hitherto resisted all attempts to compress it into a liquid. It is the lightest body in nature, and is consequently the best material for filling balloons. From its extreme lightness it is difficult to ascertain its precise density by weighing; because the presence of minute quantities of common air or watery vapour occasions considerable error. By the table of specific gravities (page 146), it appears that hydrogen gas is just 16 times lighter than oxygen, an inference derived from the composition of water to be shortly stated: it hence follows that 100 cubic inches of hydrogen gas at 60° F. and 30 inches Bar. should weigh $\frac{1}{16} \times 34.1872 = 2.1367$ grains, and that its specific gravity is 0.0689.

Hydrogen does not change the blue colour of vegetables. It is sparingly absorbed by water, 100 cubic inches of that liquid dissolving about one and a half of the gas. It cannot support respiration; for an animal soon perishes when confined in it. Death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen; since an atmosphere composed of a due proportion of oxygen and hydrogen gases may be respired without inconvenience. Nor is it a supporter of combustion; for when a lighted candle fixed on wire is passed up into an inverted jar full of hydrogen gas, the light instantly disappears.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter of combustion. This is exemplified by the experiment above alluded to, in which the gas is kindled by the flame of a candle, but burns only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a yellowish-blue flame and a very feeble light. The phenomena are different when the hydrogen is previously mixed with a due quantity of atmospheric air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant; and a flash of light passes through the mixture, followed by a violent explosion. The best proportion for the experiment is two measures of hydrogen to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by the electric spark. If a jet of hydrogen gas be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red-hot, and then sets fire to the gas, a discovery which was made in the year 1824, by Professor Doebereiner of Jena. The power of flame and electricity, in causing a mixture of hydrogen with air or oxygen gas to explode, is limited. Mr. Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air; and that a mixture of four measures of hydrogen with one of air does not explode at all. An explosive mixture, formed of two measures of hydrogen and one of oxygen gas, explodes from all the causes above enumerated. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation; for an equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause detonation, when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen; or when it is expanded to sixteen times its bulk by diminished pressure. Spongy platinum acts just as rapidly as flame or the electric spark in producing explosion, provided the gases are quite pure and mixed in the exact ratio of two to one.* Mr. Faraday finds that platinum foil, if perfectly clean, produces gradual though rather rapid combination of the gases, often followed by explosion. (Phil. Trans. 1834.)

When the action of heat, the electric spark, and spongy platinum no longer cause explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen gases unite slowly with one another, when they are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture, diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly though mixed with one hundred times their bulk of oxygen gas.

A large quantity of heat is evolved during the combustion of hydrogen gas. Lavoisier concludes from experiments made with his calorimeter, (Elements, vol. i.) that one pound of hydrogen occasions as much heat in burning as is sufficient to melt 295.6 pounds of ice. Dr. Dalton fixes the quantity of ice at 320 pounds, and Dr. Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr. Hare of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gasholders, from which a stream was made to issue through tubes communicating with each other, just before their termination. At this point the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing the two gases in due proportion into a strong metallic vessel by means of a condensing syringe, and setting fire to a jet of the mixture as it issues. An apparatus of this kind, now known by the name of the oxy-hydrogen blowpipe, was contrived by Mr. Newman, and employed by the late Professor Clarke in his experiments on the fusion of refractory substances. On opening a stop-cock which confines the compressed gases, a jet of the explosive mixture issues with force through a small blowpipe-tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube, and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which would most probably prove fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made to pass through a cylinder full of oil or water before reaching the point at which it is to burn; and Dr. Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which would be capable of intercepting the communication of flame. A modification of this apparatus has been devised by Mr. Gurney; but both his and Newman's are rendered unnecessary by the safety tube lately proposed by Mr. Hemming. It consists of a brass cylinder, about 6 inches long, and 3-4ths of an inch wide, filled with very fine brass wire in length equal to that of the tube. A pointed rod of metal, 1-8th of an inch thick, is then forcibly inserted through the centre of the bundle of wires in the tube, so as to wedge them tightly together. The interstices between the wires thus constitute very fine metallic tubes, the conducting power of which is so great as entirely to intercept the passage of flame. The mixed gases are supplied from a common bladder. (Phil. Mag. 3rd S. i. 82.) A very intense heat may be safely and easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr. Marcet. An elegant improvement on this principle has been devised by Mr. Daniell, by fixing a jet for conveying oxygen within another jet for hydrogen or coal gas, so that a current of oxygen may be introduced into the middle of the flame. (Phil. Mag. ii. 57. 3rd Series.) The heat from this apparatus is quite sufficient for most purposes; and it may be still further increased by causing the gases to pass separately through heated tubes, in order that they may have a temperature of 400° or 500° on issuing from the jets.—On this principle is founded the patent of Mr. Dunlop, of the Carron Iron Works, for increasing the temperature of blast furnaces: the air which supports the combustion is previously heated by transmission through iron tubes kept at a low red heat, whereby the power of the furnaces is surprisingly increased, and a great saving in fuel and time is accomplished.

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* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing detonation, the reader may consult the essay of M. Grotthus in the Ann. de Chimie, vol. lxxxii.; Sir H. Davy's work on Flame; Dr. Henry's essay in the Philosophical Transactions for 1824; and a paper by myself in the Edinburgh Philosophical Journal for the same year.

The compounds of hydrogen described in this section are two in number, the composition of which is as follows:—

	By Weight.			By Volume.	
	Hydrogen.	Oxygen.	Equiv.	Hyd.	Oxy.
Water (protoxide of hydrogen)	1 or 1 eq.+	8 or 1 eq.=	9	100	50
Peroxide of hydrogen	1 or 1 eq.+	16 or 2 eq.=	17	100	100

The chemical symbol of water is $H+O$, or $\dot{H}$, and sometimes Aq from aqua; and that of the peroxide is $H+2O$, or $\ddot{H}$.

WATER.

Water is the sole product of the combustion of hydrogen gas. For this important fact we are indebted to Mr. Cavendish. He demonstrated it by burning oxygen and hydrogen gases in a dry glass vessel; when a quantity of pure water was generated, exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris by Vauquelin, Fourcroy, and Seguin. Lavoisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former, added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water decomposed.

A knowledge of the exact proportions in which oxygen and hydrogen gases unite to form water, is a necessary element in many chemical reasonings. Its composition by volume was demonstrated very satisfactorily by Messrs. Nicholson and Carlisle, in their researches on the chemical agency of galvanism. On resolving water into its elements by this agent, and collecting them in separate vessels, they obtained precisely two measures of hydrogen and one of oxygen,—a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen remains after the explosion; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state, as a mean of three careful experiments, (Ann. de Ch. et de Ph. vol. xv.) that 100 parts of pure water consist of 11.1 of hydrogen and 88.9 oxygen, which is the ratio of 1 to 8.009, very nearly that of 1 to 8 above stated.

The processes for procuring a supply of hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact, that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and the hydrogen gas being set free. That the hydrogen which is evolved when zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration, that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydrogen. The product of the operation, besides hydrogen, is sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are—

Water (8 oxy. + 1 hyd.)	9
Sulphuric acid	40.1
Iron	28
Protoxide of iron (28 iron + 8 oxygen) . . .	36
Sulphate of the protoxide of iron (40.1+36) . .	76.1

Hence for every 9 grains of water which are decomposed, 1 grain of hydrogen will be set free; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of protoxide will combine with 40.1 grains of sulphuric acid, yielding 76.1 of sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the equivalent of zinc (32.3) for that of iron.—According to Mr. Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of dilute sulphuric acid on metallic zinc affords an instance of what was once called *Disposing Affinity*. Zinc decomposes pure water at common temperatures with extreme slowness; but as soon as sulphuric acid is added, decomposition of the water takes place rapidly, though the acid merely unites with oxide of zinc. The former explanation was, that the affinity of the acid for oxide of zinc disposed the metal to unite with oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the same instant. There is, as it were, but one chemical change, which consists in the combination at one and the same moment of zinc with oxygen, and of oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.

Water is a transparent colourless liquid, which has neither smell nor taste. It is a powerful refractor of light, conducts heat very slowly, and is an imperfect conductor of electricity. The experiments of Oersted, and Colladon and Sturm have proved that water is compressible by great pressure; and according to the latter observers, its absolute diminution for each atmosphere is 51.3 millionths of its volume. (An. de Ch. et de Ph. xxxvi. 140.) The relations of water, with respect to heat, are highly important; but they have already been discussed in the first part of the work. The specific gravity of water is 1, the density of all solid and liquid bodies being referred to it as a term of comparison. One cubic inch, at 62° F. and 30 inches of the barometer weighs 252.458 grains; so that it is 815 times as heavy as atmospheric air.

ter, owing partly to the extensive range of its own affinity, and partly to the nature of its elements, is one of the most powerful agents which we possess. The preparation of hydrogen gas is an example of this; and indeed there are few complex changes, where oxygen and hydrogen are present, which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many bodies. Sometimes it is contained in a variable ratio, as in ordinary solution; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates*. Thus, concentrated sulphuric acid is a compound of one equivalent of the real acid and one equivalent of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid*. The adjunct *hydro* has been sometimes used to signify the presence of water in definite proportion; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure; for if placed under the exhausted receiver of an air-pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water is much richer in oxygen gas than atmospheric air. According to the experiments of Gay-Lussac and Humboldt, it contains 34.8 per cent of oxygen, and the air separated by ebullition from rain water contains 32 per cent of that gas. All water which has once fallen on the ground becomes impregnated with more or less earthy or saline matters, and it can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Dr. Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 cubic inches of such water, at the mean temperature and pressure, absorb of

	Dalton and Henry.	Saussure.
Sulphuretted hydrogen	100 cubic inches.	253 cubic inches.
Carbonic acid	100	106
Nitrous acid	100	76
Olefiant gas	12.5	15.3
Oxygen	3.7	6.5
Carbonic oxide	1.56	6.2
Nitrogen	1.56	4.1
Hydrogen	1.56	4.6

The estimate of Saussure is in general too high. That of Drs. Dalton and Henry for nitrous oxide, according to the experiments of Sir H. Davy, is considerably beyond the truth.

PEROXIDE OF HYDROGEN.

The binoxide or peroxide of hydrogen was discovered by Thenard in the year 1818. Before describing the mode of preparing this compound, it must be observed that there are two oxides of barium; and that when the peroxide of that metal is put into a dilute acid, oxygen gas is set at liberty, and the peroxide is converted into protoxide of barium or baryta, which combines with the acid. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to a maximum of oxidation. For a full detail of all the minutiæ of the process, the reader may consult the original memoir of Thenard;[*] the general directions are the following:—To six or seven ounces of water add so much pure concentrated hydrochloric acid as is sufficient to dissolve 230 grains of baryta; and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of peroxide of barium reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effervescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, leaving the hydrochloric acid in solution. Another portion of peroxide of barium, amounting to 185 grains, is then put into the liquid: the free hydrochloric acid instantly acts upon it, and as soon as it is dissolved, the baryta is again separated as a sulphate by the addition of sulphuric acid. The solution is then filtered, in order to separate the insoluble sulphate of baryta; and fresh quantities of peroxide of barium are added in succession, till about three ounces have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The hydrochloric acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of sulphate of oxide of silver, and the sulphuric acid afterwards separated by solid baryta.

Peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed, with a vessel of strong sulphuric acid, under the exhausted receiver of an air-pump. As the water evaporates, the density of the residue increases, till at last it acquires the specific gravity of 1.452. The concentration cannot be pushed further; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

Peroxide of hydrogen, of specific gravity 1.452, is a colourless transparent liquid without odour. It whitens the surface of the skin when applied to it, causes a pricking sensation, and even destroys its texture if the application be long continued. It acts in a similar manner on the tongue; in addition to which it thickens the saliva, and tastes like certain metallic solutions. Brought into contact with litmus and turmeric paper, it gradually destroys their colour and makes them white. It is slowly volatilized *in vacuo*, a fact which shows that its vapour is much less elastic than that of water. It preserves its liquid form at all degrees of cold to which it has hitherto been exposed. At the temperature of 59° F. it is decomposed, being converted into water and oxygen gas. For this reason it ought to be preserved in glass tubes surrounded with ice.

The most remarkable property of peroxide of hydrogen is its facility of decomposition. Diffused daylight does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from escape of oxygen at 59° F., and the sudden application of a higher temperature, as that of 212°, gives rise to such rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more permanent; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is entirely decomposed. All the metals except iron, tin, antimony, and tellurium, have a tendency to decompose the peroxide of hydrogen, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium; while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

Peroxide of hydrogen is decomposed at common temperatures by many of the metallic oxides. That some protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium, and calcium may likewise be formed by the action of peroxide of hydrogen on baryta, strontia, and lime. But it is a singular fact, and I am not aware that any satisfactory explanation of it has been given, that some oxides decompose peroxide of hydrogen without passing into a higher degree of oxidation. The peroxides of lead, mercury, gold, platinum, manganese, and cobalt, possess this property in the greatest perfection, acting on peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous; oxygen gas is evolved so rapidly as to produce a kind of explosion, and such intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great even when the peroxide of hydrogen is diluted with water. Oxide of silver occasions very perceptible effervescence when put into water which contains only 1-50th of its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon peroxide of hydrogen. This effect cannot be altogether ascribed to heat disengaged during the action; for oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

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[*] In the An. de Chim. et de Phys. vol. viii. ix. x. and l.; Annals of Philosophy, vol. xiii. and xiv.; and M. Thenard's Traité de Chimie.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; let some strong acid, as the nitric, sulphuric, or hydrochloric, be then dropped into it, and the effervescence will cease on the instant. When a little finely divided gold is put into a weak solution of peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, effervescence ceases instantly; it is reproduced by the addition of potassa, and is again arrested by adding a second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as carbonic and boracic acids; or those which suffer a chemical change when mixed with peroxide of hydrogen, such as hydriodic, hydrosulphuric, and sulphurous acids. Acids appear to increase the stability of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thenard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving peroxide of barium in some dilute acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thenard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with peroxide of hydrogen.

Peroxide of hydrogen was analyzed by diluting a known weight of it with water, and then decomposing it by boiling the solution. According to two careful analyses, conducted on this principle, 864 parts of the peroxide are composed of 466 of water, and 398 of oxygen gas. The 466 of water contain 414 of oxygen, whence it may be inferred that peroxide of hydrogen contains twice as much oxygen as water. A small deficiency of oxygen in this experiment was to be expected, owing to the difficulty of obtaining peroxide of hydrogen perfectly free from water.

SECTION V.

NITROGEN.

The existence of nitrogen gas, as distinct from every other gaseous substance, appears to have been first noticed in the year 1772 by the late Dr. Rutherford of Edinburgh. Lavoisier discovered in 1775 that it is a constituent part of the atmosphere; and the same discovery was made soon after, or about the same time, by Scheele. Lavoisier called it *azote* from *a privative*, and ζωὴ life, because it is unable to support the respiration of animals; but as it possesses this negative property in common with most other gases, the more appropriate term *nitrogen* has been since applied to it, from the circumstance of its being an essential ingredient of nitric acid.

Nitrogen is most conveniently prepared by burning a piece of phosphorus in a jar full of air inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, metaphosphoric acid is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potassa. Several other substances may be employed for withdrawing oxygen from atmospheric air. A solution of protosulphate of iron, charged with binoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in twenty-four hours, if exposed to a temperature of 60° F. A solution of sulphuret of potassium or calcium acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness. Nitrogen gas may likewise be obtained by exposing a mixture of fresh muscle and nitric acid of specific gravity 1.20 to a moderate temperature. Effervescence then takes place, and a large quantity of gaseous matter is evolved, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime-water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and will be considered more conveniently in a subsequent part of the work.

Pure nitrogen is a colourless gas, wholly devoid of smell and taste. It does not change the blue colour of vegetables, and is distinguished from other gases more by negative characters than by any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen; though, under favourable circumstances, it may be made to unite with oxygen. Water, when deprived of air by ebullition, takes up about one and a half per cent of it. Its specific gravity is estimated at 0.976 by Dulong and Berzelius, and 0.9722 by Dr. Thomson: I have adopted 0.9727 as more consistent with the specific gravity of air and oxygen gas. Hence 100 cubic inches at the mean temperature and pressure will weigh 30.1650 grains.

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound; and this opinion has been warmly advocated by Sir H. Davy and Berzelius. The chief argument in favour of this view drawn from the phenomena that attend the formation of what is called *ammoniacal amalgam*. From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal; and as the only method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its small specific gravity, can hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the supposed metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under galvanic influence than its elements begin to separate spontaneously, and in a few minutes decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Sir H. Davy accounted for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen by uniting with the supposed metal; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thenard (Recherches Physico-Chimiques, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture; and they infer from their experiments that it is composed of those three substances combined directly with each other. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen; nor was Sir H. Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success. Berzelius has defended the idea that nitrogen is a compound body on other principles; but as his arguments, though very ingenious, are merely speculative, they cannot be admitted as decisive of the question.

Chemists are not agreed about the equivalent of nitrogen. In this country 14 is commonly adopted; but from the experiments of Berzelius, with which my own observations correspond (Phil. Trans. 1833), 14.15 is a better estimate. The compounds of nitrogen treated of in this section are the following, exclusive of atmospheric air, which is regarded as a mechanical mixture:—

	By Volume.		By Weight.			
	Nit.	Oxy.	Nit.	Oxy.	Equiv.	Symbols.
Nitrous oxide	100	50	14.15	+ 8	= 22.15	$N+O$ or $\dot{N}$
Nitric oxide	100	100	14.15	+ 16	= 30.15	$N+2O$ or $\ddot{N}$
Hyponitrous acid	100	150	14.15	+ 24	= 38.15	$N+3O$ or $\dddot{N}$
Nitrous acid	100	200	14.15	+ 32	= 46.15	$N+4O$ or $\ddddot{N}$
Nitric acid	100	250	14.15	+ 40	= 54.15	$N+5O$ or $\overset{\cdot\cdot\cdot}{\ddot{N}}$.

THE ATMOSPHERE.

The earth is everywhere surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible, excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. Its specific gravity is unity, being the standard with which the density of all gaseous substances is compared. It is 815 times lighter than water, and nearly 11065 times lighter than mercury. The knowledge of its exact weight is an essential element in many physical and chemical researches, and has been lately determined with very great care by Dr. Prout. According to his observations 100 cubic inches of pure and dry atmospheric air, at 60° F. and 30 B., weigh 31.0117 grains.

The pressure of the atmosphere was first noticed early in the seventeenth century by Galileo, and was afterwards demonstrated by his pupil Torricelli, to whom science is indebted for the invention of the barometer. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and is capable of supporting a column of water 34 feet high, and one of mercury of 30 inches; that is, a column of mercury one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of equal base and 34 feet long, and as a column of air of equal base reaching from the level of the sea to the extreme limit of the atmosphere. By the use of the barometer it was discovered that the atmospheric pressure is variable. It varies according to the elevation above the level of the sea, and on this principle the height of mountains is estimated. Supposing the density of the atmosphere to be uniform, a fall of one inch in the barometer would correspond to 11065 inches, or 922 feet of air; but in order to make the calculation with accuracy, allowance must be made for the increasing rarity of the air, and for various other circumstances which are detailed in works on meteorology. (Daniell's Meteorological Essays, 2d edit. 376.) From causes at present not understood, the pressure varies likewise at the same place. On this depends the indications of the barometer as a weather-glass; for observation has fully proved, that the weather is commonly fair and calm when the barometer is high, and usually wet and stormy when the mercury falls.

Atmospheric air is highly compressible and elastic, so that its particles admit of being approximated to a great extent by compression, and expand to an extreme degree of rarity, when the tendency of its particles to separate is not restrained by external force. It has been found experimentally that the volume of air and all other gaseous fluids, so long as they retain the elastic state, is inversely as the pressure to which they are exposed. Thus a portion of air which occupies 100 measures when compressed by a force of one pound, will be diminished to 50 measures when the pressure is doubled, and will expand to 200 measures when the compression is equal to half a pound. This law was first demonstrated in 1662 by the celebrated Boyle, and a second demonstration of it was given some years afterwards by the French philosopher M. Mariotte, apparently without being aware that the discovery had been previously made in England. It is hence frequently called the law of Mariotte. Till lately it had not been verified for very great pressures; but from the experiments of Oersted in 1825, who extended his observations to air compressed by a force equal to 110 atmospheres, it may be inferred to be quite general, except when the gaseous matter assumes the liquid form. (Edinburgh Journal of Science, iv. 224.) It has, indeed, been recently stated by M. Despretz that the easily condensible gases vary from this law, diminishing under increase of pressure much more rapidly than atmospheric air; but the details of his experiments have not, I believe, been published.* (An. de Ch. et de Ph. xxxiv. 335 and 433.) At what pressure air becomes liquid is uncertain, since all attempts to condense it have hitherto been unsuccessful.

The extreme compressibility and elasticity of the air account for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side; and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarified ones to ascend. The motion of air gives rise to various familiar phenomena. A stream or current of air is wind, and an undulating vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious from the consideration, that those portions which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part. The atmospheric column diminishes in length as the distance from the earth's surface increases; and, consequently, the greater the elevation, the lighter must be the air. It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles; and Dr. Wollaston estimated, from the law of expansion of gases, that it must extend to at least 40 miles with properties unimpaired by rarefaction. In speculating on its extent beyond that distance, it becomes a question whether the atmosphere is or is not limited to the earth. This subject was discussed with his usual sagacity by the late Dr. Wollaston in an essay on the Finite Extent of the Atmosphere, published in the Philosophical Transactions for 1822. On the supposition that the atmosphere is unlimited, it would pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which would depend on their respective forces of attraction. Now Dr. Wollaston inferred from astronomical observations made by himself and Captain Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same inference with respect to the planet Jupiter. If the accuracy of these conclusions be admitted, it follows that our atmosphere is confined to the earth; and it may next be asked, by what means is its extent limited? Dr. Wollaston accounted for it by supposing the air, after attaining a certain degree of rarefaction, to possess such feeble elasticity, that the tendency of its particles to separate further from each other is counteracted by gravity. The unknown height at which this equilibrium between the two forces of elasticity and gravitation takes place, is the extreme limit of the atmosphere.

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* See note, page 53.—*Ed.*

The loss of elasticity may be ascribed to two powerful and concurring causes; namely, to the distance between the particles of air when highly rarefied, and to the extreme cold which prevails in the higher strata of the atmosphere.

The temperature of the atmosphere varies with its elevation. Gaseous fluids permit radiant matter to pass freely through them without any absorption, and, therefore, without their temperature being influenced by its passage. The atmosphere is not heated by transmitting the rays of the sun, but receives its heat solely from the earth, and chiefly by actual contact; so that its temperature becomes progressively lower, as the distance from the general mass of the earth increases. Another circumstance which contributes to the same effect, is the increasing tenuity of the atmosphere; for the temperature of rarefied air is less raised by a given quantity of heat, than that of the same portion of air when compressed, owing to its specific heat being greater in the former state than in the latter. From the joint influence of both these causes it is found that, in ascending into the atmosphere, the temperature diminishes at the rate of one degree for about every 352 feet. The rate of decrease is probably much slower at considerable distances from the earth; but still there is no reason to doubt that the temperature continues to decrease with the increasing elevation. There must consequently in every latitude be a point, where the thermometer never rises above 32°, and where ice is never liquefied. This point varies with the latitude, being highest within the tropics and descending gradually as we advance towards the poles. The following table, from the Supplement to the Encyclopedia Britannica, page 190, article Climate, shows the point of perpetual ice corresponding to different latitudes.

Latitude.	English feet in height.	Latitude.	English feet in height.
0°	15,207	45°	7,671
5°	15,095	50°	6,334
10°	14,764	55°	5,034
15°	14,220	60°	3,818
20°	13,478	65°	2,722
25°	12,557	70°	1,778
30°	11,484	75°	1,016
35°	10,287	80°	457
40°	9,001	85°	117

Air was one of the four elements of the ancient philosophers, and their opinion of its nature prevailed generally, till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of sulphuret of potassium, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron wire and phosphorus.

The earlier analyses of the air did not agree very well with each other. According to the researches of Lavoisier, it is composed of 27 measures of oxygen and 73 of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from 20 to 25 per cent; and Cavendish estimated it only at 20. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Cavendish. The results of Scheele and Priestley are clearly referrible to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemists were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if sulphuret of potassium be dissolved in that liquid by the aid of heat, the solution, when agitated with air, takes up a portion of nitrogen, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the sulphuret in cold unboiled water. The binoxide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but for reasons which will soon be mentioned, its indications are very apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th, for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures of pure atmospheric air consist of 20 or 21 volumes of oxygen, and 80 or 79 of nitrogen. The most approved mode of analysis consists in mixing with the air, a quantity of hydrogen sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. The combination may also be effected without detonation by means of spongy platinum. Water is formed, and is condensed, and since that liquid is composed of one volume of oxygen and two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others.*

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* The best analyses of atmospheric air correspond so nearly with the proportions of two volumes of nitrogen to half a volume of oxygen, that it seems probable that these proportions (which correspond at the same time with the theory of volumes) would be obtained exactly, if our experiments could be performed with rigid accuracy. On the assumption that these are the true proportions, the specific gravity of oxygen would be 1.1111, and that of nitrogen 0.9722; numbers which correspond very nearly with those contained in the table, page 146 and with the experimental results of Berzelius and Dulong. The composition of atmospheric air, when stated in volumes, gives the oxygen at 20 per cent, as mentioned by Dr. Turner; and yet the usual analyses make it 21 per cent. This discrepancy will probably disappear when the analysis is performed with more accuracy. Dr. Hare found that the average of a great number of analyses of atmospheric air performed by explosion with hydrogen, by means of his very accurate eudiometers, gave the proportion of oxygen at 20.66 per cent, which approaches very nearly to the quantity indicated by the theory of volumes.—*Ed.*

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odoriferous matter of flowers and other volatile substances, which are also frequently present. Saussure found carbonic acid in air collected at the top of Mont-Blanc; and it exists at all altitudes which have been hitherto attained. Saussure in a recent essay, states the proportion of this gas to vary at the same place within short intervals of time. It is greater in summer than in winter; and from observations made during spring, summer, and autumn, in the open fields and in calm weather, its proportion is inferred to be always greater at night than in the day, and to be more abundant in gloomy than in bright weather. A very moist state of the ground, as after much rain, diminishes the quantity of carbonic acid, apparently by direct absorption. It is rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; but its quantity is there nearly the same in day and night, in wet and dry weather, because the higher strata of the air are less influenced by vegetation, and the state of the soil. Saussure thinks also that a highly electrical state of the atmosphere tends to diminish the quantity of carbonic acid. He found that 10,000 parts of air contain 4.9 of carbonic acid as a mean, 6.2 as a maximum, and 3.7 as a minimum. (An. de Ch. et de Ph. xxxviii. 411. xliv. 5.)

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of the nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air, at different times, and in different places, depends on the relative quantity of this gas. It was, therefore, supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered by determining the proportion of oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discordant results of the earlier analysts, was soon proved to be fallacious. It appears, on the contrary, that the composition of the air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont-Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition as that collected at a short distance from its surface. Even the miasmata of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtile a nature to be detected by chemical means, and not to a deficiency of oxygen. Seguin examined the infectious atmosphere of an hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed whether the oxygen and nitrogen gases of the atmosphere are simply intermixed, or chemically combined with each other. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and, therefore, it might be expected, were they merely mixed together, that the oxygen as the heavier gas ought, in obedience to the force of gravity, to collect in the lower regions of the air; while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube, preserved at perfect rest, its upper part will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper with nitrogen, these gases will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are nearly in the simple ratio of 1 to 4, which agrees with the law of combination by volume; and by weight they are as 8 to 28.30, which corresponds to one equivalent of oxygen and two of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen abstract it from the atmosphere with as much facility as if the nitrogen were absent altogether. Even water effects this separation; for the air which is expelled from rain water by ebullition, contains more than 21 per cent of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of 1 to 4, the mixture occupies precisely 5 volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen gases ought to possess; and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, iv. 211.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. It has been conceived that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, might still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and defended by the late Dr. Murray. This doctrine, however, is not satisfactory. It is, indeed, quite conceivable that oxygen and nitrogen may attract each other in the way supposed; and it may be admitted that this supposition explains why these two gases continue in a state of perfect mixture. But still the explanation is unsatisfactory; and for the following reason:—Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpendicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid gas in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue; the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now this result cannot be ascribed to the action of affinity. Carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and, therefore, it is gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with each other, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is twenty-two times lighter than itself, it will surely explain why oxygen and nitrogen gases, the densities of which differ so little, should be intermingled in the atmosphere.

The explanation which Dalton has given of these phenomena is founded on the assumption, that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. It follows, from this supposition, that one gas acts as a vacuum with respect to another; and, therefore, if a vessel full of carbonic acid be made to communicate with another of hydrogen, the particles of each gas insinuate themselves between the particles of the other, till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum, because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vessel of hydrogen had been a vacuum. (Manchester Memoirs, vol. v.)

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other. This view receives support from the experiments of Mr. Graham of Glasgow on the diffusion of gases. (Phil. Trans. Edin. 1831.) When a gas is contained in a glass bell jar which has a crack or fissure in its sides, or communicates with the air by a narrow aperture, or is contained in a porous vessel, the gas gradually diffuses itself into the air, and air into the gas, each passing through the chink or other small opening at the same time, but in opposite directions. On ascertaining after an interval how much gas has escaped from, and how much air entered into, the vessel, it will be found that the respective quantities depend on the relative densities; and the same principle of intermixture equally applies when the apertures of communication are large, as when they are small. Each gas has a diffusiveness peculiar to itself, and which is greater as its density is less. Mr. Graham determined the rate of diffusion for different gases by means of what he calls a *diffusion tube*, which is simply a graduated tube closed at one end by plaster of Paris, a substance, when moderately dry, possessed of the requisite porosity. He has been led by direct experiment to the following conclusion,—that "the diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely small volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas." The relative diffusiveness of each gas may hence be represented by the reciprocal of the square root of its density. Thus, the density of air being 1, its diffusiveness is 1 also; that of hydrogen is

$$\frac{1}{\sqrt{0.069}} = \frac{1}{0.2627} = 3.807; \text{ that of oxygen } \frac{1}{\sqrt{1.102}} = \frac{1}{1.05} = 0.9524;$$

$$\text{and that of nitrogen } \frac{1}{\sqrt{0.972}} = 1.014;$$

so that the relative power of diffusion of air, hydrogen, oxygen, and nitrogen, is indicated by the numbers, 1, 3.807, 0.9524 and 1.014. In gases which are very sparingly soluble in water, and hence not condensible by the moisture of the plaster of Paris, the results of experiment coincide so exactly with the law, that Mr. Graham suggests its application to determine the density of gases. Thus if g denote the diffusiveness of a gas, as found by careful experiment, and d its density; then since, by the law of diffusion,

$$g = \frac{1}{\sqrt{d}}, \text{ we have } d = \frac{1}{g^2}$$

It is obvious that these phenomena cannot be referred to any chemical principle, but are dependent on the mechanical constitution of gases. It has been lately shown in a very clever paper by Mr. Thomas Thomson of Clitheroe (Phil. Mag. 3rd Series, iv. 321), that the law of gaseous diffusion is included under Dalton's hypothesis, that one gas is as a vacuum with respect to another. For it is a law deduced from the physical properties of gaseous bodies, that the velocities of gases flowing under like circumstances into a vacuum are inversely as the square roots of their densities, which is precisely the same law that regulates their flow into each other. *

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* As connected with this subject, the reader is referred to an important paper on the "Penetrativeness of Fluids," by Dr. J. K. Mitchell, of Philadelphia, published in the American Journal of Medical Sciences vol. vii. p. 36.—*Ed.*

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that its quantity would gradually diminish, unless the tendency of those causes were counteracted by some compensating process. To all appearance there does exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbonaceous part of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is eliminated; but it follows from the experiments of Priestley, Davy, and Dr. Daubeny, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned is uncertain. From the great extent of the atmosphere, and the continual agitation to which its different parts are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals.

PROTOXIDE OF NITROGEN.

This gas was discovered by Priestley, who gave it the name of *dephlogisticated nitrous air*. Sir H. Davy called it *nitrous oxide*. According to the principles of chemical nomenclature, its proper appellation is *protoxide of nitrogen*. It may be formed by exposing nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen, when the nitric oxide loses one-half of its oxygen, and is converted into the protoxide. But the most convenient method of procuring it is by means of nitrate of ammonia. This salt is prepared by neutralizing with carbonate of ammonia pure nitric acid diluted with about three parts of water, and concentrating by evaporation until a drop of the liquid let fall on a cold plate becomes a firm mass, adding a little ammonia towards the close to ensure neutrality. The salt after cooling is broken to pieces, introduced into a retort, and heated by a lamp or pan of charcoal: at first, below 400°, fusion ensues; and as the heat rises to 480° or 500° rapid decomposition sets in, which continues until all the salt disappears. If a white cloud appears within the retort, due to some of the salt subliming undecomposed, the heat should be checked.

The sole products of this operation, when carefully conducted, are water and protoxide of nitrogen. The nature of the change will be readily understood by comparing the composition of nitrate of ammonia with that of the products derived from it. These, in round numbers, are as follows:—

Nitric Acid.	Ammonia.	Water.	Prot. of Nitrogen.
Nitrogen 14 or 1 eq.	Nitrogen 14 or 1 eq.	Hyd. 3 or 3 eq.	Nit. 28 or 2 eq.
Oxygen 40 or 5 eq.	Hydrogen 3 or 3 eq.	Oxy. 24 or 3 eq.	Oxy. 16 or 2 eq.
54	17	27	44

The same expressed in symbols is

$N+5O$; $N+3H$; | $3(H+O)$; $2(N+O)$.

It thus appears that the hydrogen in the ammonia takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into protoxide of nitrogen: 71 grains of the salt will thus yield 44 grains of protoxide of nitrogen and 27 of water.

Protoxide of nitrogen is a colourless gas, which does not affect the blue vegetable colours, even when mixed with atmospheric air. Recently boiled water, which has cooled without exposure to the air, absorbs nearly its own bulk of it at 60° F. and gives it out again unchanged by boiling. The solution, like the gas itself, has a faint agreeable odour and sweet taste. The action of water upon it affords a ready means of testing its purity; removing it readily from all other gases, such as oxygen and nitrogen, which are sparingly absorbed by that liquid. For the same reason it cannot be preserved over cold water; but should be collected either over hot water or mercury.

Protoxide of nitrogen is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if immersed while the combustion is lively, the size of the flame is considerably increased. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases, the product of combustion is the same as when oxygen gas or atmospheric air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. Protoxide of nitrogen suffers decomposition when a succession of electric sparks is passed through it, and a similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved, in both instances, into nitrogen, oxygen, and nitrous acid.

Sir H. Davy discovered that protoxide of nitrogen may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed nine quarts of it, contained in a silk bag, for three minutes, and 12 quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations are followed by most agreeable feelings of excitement, similar to the earlier stages of intoxication. This is shown by a strong propensity to laughter, by a rapid flow of vivid ideas, and an unusual disposition to muscular exertion. These feelings, however, soon subside; and the person returns to his usual state without experiencing the languor or depression which so universally follows intoxication from spirituous liquors. Its effects, however, on different persons are various; and in individuals of a plethoric habit, it sometimes produces giddiness, headach, and other disagreeable symptoms. (Researches on the Nitrous Oxide.)

Protoxide of nitrogen was analyzed by Sir H. Davy by means of hydrogen gas. He mixed 39 measures of the former with 40 measures of hydrogen, and fired the mixture by the electric spark. Water was formed; and the residual gas, which amounted to 41 measures, had the properties of pure nitrogen. As 40 measures of hydrogen require 20 of oxygen for combustion, it follows that 39 volumes of the protoxide of nitrogen contain 41 of nitrogen and 20 of oxygen. But since no exception has hitherto been found to Gay-Lussac's law of gaseous combination, it may be inferred that protoxide of nitrogen contains its own bulk of nitrogen and half its volume of oxygen. The analysis of this compound by Dr. Henry, (Annals of Phil. viii. 299, N. S.) performed by means of carbonic oxide gas, has proved beyond a doubt that this is the exact proportion. Now,

100 cubic inches of nitrogen gas weigh .	30.1650 grains.
50 do. oxygen	17.0936
These numbers added together amount to .	47.2586

which must be the weight of 100 cubic inches of the protoxide; and its specific gravity is, therefore, 1.5239. Its composition by weight is determined by the same data, being 17.0936 of oxygen to 30.1650 of nitrogen, or as 8 to 14.12, nearly the number already stated. (Page 167)

BINOXIDE OF NITROGEN.

This compound is best obtained by the action of nitric acid, of specific gravity 1.2, on metallic copper. Brisk effervescence takes place without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires a beautiful blue colour, and yields on evaporation a salt which is composed of nitric acid and oxide of copper. The chemical changes that occur are the following.—One portion of nitric acid suffers decomposition: part of its oxygen oxidizes the copper; while another part is retained by the nitrogen of the nitric acid, forming binoxide of nitrogen. The oxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate of copper. Many other metals are oxidized by nitric acid, with disengagement of a similar compound; but none, mercury excepted, yields so pure a gas as copper.

The gas derived from this source was discovered by Dr. Hales. It was first carefully studied by Priestley, who called it *nitrous air*. The terms *nitrous gas* and *nitric oxide* are frequently applied to it; but *binoxide of nitrogen*, as indicative of its nature, is the most suitable appellation.

Binoxide of nitrogen is a colourless gas. When mixed with atmospheric air, or any gaseous mixture that contains oxygen in an uncombined state, dense, suffocating, acid vapours, of a red or orange colour, are produced, called *nitrous acid vapours*; which are copiously absorbed by water, and communicate acidity to it. This character serves to distinguish the binoxide from every other substance, and affords a convenient test of the presence of free oxygen. Though it gives rise to an acid by combining with oxygen, binoxide of nitrogen itself does not redden the blue colour of vegetables; but for this experiment, the gas must be previously well washed with water to separate all traces of nitrous acid. Water absorbs the binoxide sparingly;—100 measures of that liquid, cold and recently boiled, take up about 11 of the gas.

Very few inflammable substances burn in binoxide of nitrogen. Burning sulphur and a lighted candle are instantly extinguished by it. Charcoal and phosphorus, however, if in a state of vivid combustion at the moment of being immersed in it, burn with increased brilliancy. The product of the combustion is carbonic acid in the former case, and metaphosphoric acid in the latter, nitrogen being separated in both instances. With an equal bulk of hydrogen, it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a greenish-white flame, water and pure nitrogen gas being the sole products. The action of freshly ignited spongy platinum on a mixture of hydrogen and binoxide of nitrogen gases leads to the slow production of water and ammonia.

Binoxide of nitrogen is quite irrespirable, exciting strong spasm of the glottis, as soon as an attempt is made to inhale it. The experiment, however, is a dangerous one; for if the gas did reach the lungs, it would there mix with atmospheric air, and be converted into nitrous acid vapours, which are highly irritating and corrosive.

Binoxide of nitrogen is partially resolved into its elements by being passed through red-hot tubes. A succession of electric sparks has a similar effect. It is converted into protoxide of nitrogen by substances which have a strong affinity for oxygen, such as moist iron filings, and a solution of sulphuret of potassium. Sir H. Davy ascertained its composition by the combustion of charcoal. (Elements of Chemical Philosophy, p. 200.) Two volumes of the binoxide yielded one volume of nitrogen, and about one of carbonic acid, whence it was inferred to consist of equal measures of oxygen and nitrogen gases united without any condensation. Gay-Lussac, in his essay in the *Memoires d'Arcueil*, proved that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; when 50 measures of pure nitrogen were left, and the potassa formed corresponded to 50 measures of oxygen. The same fact has been lately proved by Dr. Henry (An. of Phil. N. S. viii. 299.) Hence, as

50 cubic inches of oxygen gas weigh	17.0936 grains.
50 do. nitrogen	15.0825
100 cubic inches of the binoxide must weigh	32.1761

Its composition stated at page 167 is drawn from these facts. Its density ought to be 1.0375, which closely agrees with the direct experiments of Davy, Thomson, and Bérard.

From the invariable formation of red-coloured acid vapours, whenever binoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty; and since the product is wholly absorbed by water, either of them may be entirely removed from any gaseous mixture by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them in one proportion only; and inferring on this supposition, that a given absorption must always indicate the same quantity of oxygen, he was led to employ binoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results obtained by this method, soon excited suspicion of their accuracy; and the source of error has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Dalton, that for 100 measures of oxygen, 400 of the binoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the binoxide, corresponding to 100 of oxygen, is exceedingly variable. It does not follow from this, that oxygen and binoxide of nitrogen unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds, hyponitrous, nitrous, and nitric acids; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two, if not all, are generated at the same time, and in a proportion to each other which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and binoxide of nitrogen is made over water, are the following:—1, The diameter of the tube; 2, The rapidity with which the mixture is made; 3, The relative proportion of the two gases; 4, The time allowed to elapse after mixing them; 5, Agitation of the tube; and lastly, The opposite conditions of adding the oxygen to the binoxide, or the binoxide to the oxygen.

Notwithstanding these many sources of error, Dalton and Gay-Lussac maintain that binoxide of nitrogen may nevertheless be employed in Eudiometry; and they have described the precautions which are required to ensure accuracy. Dalton has given his process in the Annals of Philosophy, x. 38; and further directions have been published by Dr. Henry in his Elements. The method of Gay-Lussac, to which my own observation would lead me to give the preference, may be found in the *Memoires d'Arcuiel*, ii. 247. Instead of employing a narrow tube, such as is commonly used for measuring gases, Gay-Lussac advises that 100 measures of air should be introduced into a very wide tube or jar, and that an equal volume of binoxide of nitrogen should then be added. The red vapours, which are instantly produced, disappear very quickly; and the absorption after half a minute, or a minute at the most, may be regarded as complete. The residue is then transferred into a graduated tube and measured. The diminution almost always, according to Gay-Lussac, amounts to 84 measures, one-fourth of which is oxygen.* Gay-Lussac has applied this process to the analysis of various mixed gases, in which the oxygen was sometimes in a greater, at others in a less proportion than in the atmosphere, and the indications were always correct. When the proportion of oxygen is great, a proportionally large quantity of the binoxide must, of course, be employed, in order that an excess of it may be present.

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* On the supposition that the oxygen and binoxide of nitrogen unite in the proportion to form nitrous acid, one-third, and not one-fourth, of the di-

There is another mode of absorbing oxygen gas by means of binoxide of nitrogen. If a current of the binoxide be conducted into a solution of protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in Eudiometry; because the absorption of oxygen is accompanied, or at least very soon followed, by evolution of gas from the liquid itself.

Sir H. Davy ascertained that binoxide of nitrogen is dissolved, without decomposition, by a cold solution of protosulphate of iron; and that when the solution is heated, the greater part of the gas is disengaged, and the remainder decomposed. The decomposition is determined chiefly by the affinity of protoxide of iron for oxygen gas. The protoxide of iron decomposes a portion of water and binoxide of nitrogen at the same time, and unites with the oxygen of both; while the hydrogen of the water and nitrogen of the binoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise.

It is singular that both binoxide and protoxide of nitrogen, notwithstanding the absence of acidity, are capable of forming compounds of considerable permanence with the pure alkalies. The circumstances which give rise to the formation of these compounds will be stated in the description of nitre.

HYPONITROUS ACID.

On adding binoxide of nitrogen in excess to oxygen gas, confined in a glass tube over mercury, Gay-Lussac observed that the absorption is always uniform, provided a strong solution of pure potassa is put into the tube before mixing the two gases. He found that 100 measures of oxygen gas combine under these circumstances with 400 of the binoxide, forming an acid which unites with the potassa. The compound so formed is hyponitrous acid, the composition of which may be easily inferred from the proportions just mentioned. For as binoxide of nitrogen contains half its volume of oxygen gas, the new acid must be composed of 200 measures of nitrogen and 300 of oxygen, or of 100 and 150, as already stated (page 167).

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minution ought to be due to oxygen; for nitrous acid is composed of one volume of oxygen and two volumes of binoxide of nitrogen. It may be asked, therefore, what are the real products of the experiment; as in point of fact, one-fourth of the gaseous matter which disappears is due to oxygen? The late Dr. Dana ingeniously reconciled this result with the theory of volumes, by supposing that two-thirds of the binoxide of nitrogen become hyponitrous acid, and one-third nitrous acid. Thus supposing six volumes of the binoxide to be mixed with a sufficient quantity of oxygen, four volumes are assumed to be converted into hyponitrous acid, by combining with one volume of oxygen, and the remaining two, into nitrous acid, by uniting with the same quantity of oxygen. In this manner six volumes of binoxide and two volumes of oxygen, in all eight volumes, will disappear, being condensed, as above explained, into hyponitrous and nitrous acids. Now of these eight volumes, it is apparent that one-fourth is oxygen.

When the experiment is performed with certain precautions, nitrous acid is the sole product, and the formula for calculating the quantity of oxygen is of course to divide the diminution by three. I had the pleasure of seeing this proved experimentally, on several occasions, by Dr. Hare of the University of Pennsylvania.—*Ed.*

Another method of forming it is by keeping binoxide of nitrogen for a considerable time, say three months, in a glass tube over mercury, with a strong solution of pure potassa. The binoxide is resolved into hyponitrous acid, which unites with the alkali, and protoxide of nitrogen remains in the tube It is also said to be formed when 400 measures of binoxide of nitrogen are mixed with 100 of oxygen gas, both quite dry, and the resulting orange fumes are exposed to a cold of 0° F. when it is condensed into a liquid.

Anhydrous liquid hyponitrous acid is colourless at 0° F. and green at common temperatures. It is so volatile, that in open vessels the green fluid wholly and rapidly passes off in the form of an orange vapour, which is said by Mitscherlich to have a density of 1.72. On admixture with water it is converted into nitric acid and binoxide of nitrogen, the latter escaping with effervescence; but when much nitric acid is present, the hyponitrous is changed into nitrous acid, the presence of which imparts several shades of colour, orange, yellow, green, and blue, according as its quantity is more or less predominant. One equivalent of hyponitrous and one of nitric acid yield two equivalents of nitrous acid: thus $N + 3O$ and $N + 5O$ obviously contain the elements for forming $2(N + 4O)$.

Hyponitrous acid does not unite directly with alkalies, being then resolved principally into nitric acid and binoxide of nitrogen; but the hyponitrites of the alkalies and alkaline earths may be obtained by heating the corresponding nitrates to a gentle red heat; and the hyponitrite of the oxide of lead is formed by boiling a solution of the nitrate of that oxide with metallic lead.

Hyponitrous acid forms with water and sulphuric acid a crystalline compound, which is generated in large quantity during the manufacture of sulphuric acid, and the production of which is an essential part of that process. It is generated whenever moist sulphurous acid gas and nitrous acid vapour are intermixed, being instantly deposited in the form of white acicular crystals; and Gay-Lussac discovered that it may also be made by the direct action of anhydrous nitrous and strong sulphuric acid. The first attempt to determine its composition analytically was by Dr. Henry, who found it to consist of one equivalent of hyponitrous acid, five of sulphuric acid, and five of water. (Ann. of Phil. xxvii. 367.) Gaultier de Claubry has lately repeated the analysis of the same compound in a state of more perfect dryness, and by what he considers a better method; and he gives as its constituents two equivalents of hyponitrous acid, four of water, and five of sulphuric acid. (An. de Ch. et de Ph. xlv. 284.) The theory of its production has been very carefully studied by G. de Claubry. It appears that when moist sulphurous and nitrous acids react on each other, the former is converted into sulphuric and the latter into hyponitrous acid, the oxygen lost by one being gained by the other. A little nitrogen gas is always disengaged at the same time, which can only arise from a small portion of nitrous acid losing the whole of its oxygen. The action of sulphuric on nitrous acid is different: in this case the nitrous acid is resolved into nitric and hyponitrous acids, the latter uniting with sulphuric acid and most of its water to produce the crystalline solid, while the remainder of the water unites with the nitric acid. When the crystalline matter is put into water, the hyponitrous is resolved into nitrous acid and binoxide of nitrogen, both of which escape with effervescence. If much water is present, more or less of the nitrous acid is converted into nitric acid and the binoxide. Similar changes ensue when the crystals are exposed to the air, humidity being rapidly absorbed. This subject has also been lately examined by Bussy with similar results.

NITROUS ACID.

To form pure nitrous acid by the mixture of oxygen gas with binoxide of nitrogen, the operation should not be conducted over water or mercury: the presence of the former determines the production of nitric acid, and the latter is oxidized by the nitrous acid, and, therefore, decomposes it. Davy showed, by making the mixture in a dry glass vessel previously exhausted, that nitrous acid vapour is formed by the action of 200 measures of binoxide of nitrogen on 100 of oxygen gas; and hence, as 200 of the binoxide contain 100 of nitrogen and 100 of oxygen, nitrous acid was inferred to consist of 100 measures of nitrogen united with 200 of oxygen gas, as stated at page 167. This inference has been confirmed by the researches of Gay-Lussac and Dulong (An. de Ch. et de Ph. i. and ii.), the former of whom also proved that its elements contract to 1-3rd of their volume; or in other words, 100 measures of nitrous acid vapour contain 100 of nitrogen gas and 200 of oxygen. The specific gravity of this vapour ought to be 3.1775, formed of 0.9727 the sp. gr. of nitrogen + 2.2048 twice the sp. gr. of oxygen.

Nitrous acid vapour is characterized by its orange-red colour, acid reaction to test paper, and by being absorbed by water with disengagement of binoxide of nitrogen and formation of nitric acid. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid may exist in the liquid as well as in the gaseous form. Its vapour may be condensed by a freezing mixture; but the best mode of preparing it, is by exposing, in an earthen retort, nitrate of lead, carefully dried, to a red heat. The nitric acid of the salt is resolved into nitrous acid and oxygen; and on receiving these products in a dry tube surrounded by a mixture of ice and salt, most of the former is condensed. The liquid as thus obtained is anhydrous, is acid and pungent to the taste, gives a yellow stain to the skin, and is powerfully corrosive. At common temperatures its colour is an orange-red; but it becomes yellow when cooled below 32°, and at 0° F. is nearly colourless. Its density is 1.451. It is extremely volatile, boiling at 82°: in a stoppered bottle it preserves its liquid form at common temperatures; but when exposed to the atmosphere it is rapidly dissipated, forming nitrous acid vapours which, when once mixed with air or other gases, require intense cold for condensation.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The acid is decomposed at the same time, being commonly changed into binoxide of nitrogen, though sometimes the protoxide and even pure nitrogen gases are evolved. When transmitted through a red-hot porcelain tube, it suffers decomposition, and a mixture of oxygen and nitrogen gases is obtained.

When nitrous acid is mixed with a considerable quantity of water, it is instantly resolved into nitric acid, which unites with the water, and binoxide of nitrogen which escapes with effervescence. Three equivalents of nitrous acid are in proportion to form two of nitric acid and one of the binoxide; for $3(N+4O)$ contain $2(N+5O)$ and $N+2O$. When a rather small quantity of water is used, the disengagement of binoxide of nitrogen, at first considerable, becomes less and less as successive quantities of nitrous acid are added, till at last the evolution of gas ceases altogether. The colour of the solution varies remarkably during the process: from being colourless, the liquid acquires a blue tint, then passes into bluish-green, green, yellow, and lastly orange. These different solutions contain different relative quantities of nitric acid, nitrous acid, and water, on which circumstance the varying shades of colour depend. Nitric and nitrous acids are disposed to unite with each other, and the influence of this attraction enables nitrous acid to sustain admixture with water without decomposition. Strong nitric acid will unite with a considerable quantity of nitrous acid, and thereby acquires an orange-red tint. In a weaker nitric acid the water decomposes part of the nitrous acid, and the colour of the solution is orange or yellow. As the strength of the nitric acid becomes weaker and weaker, the quantity of nitrous acid which it can protect from decomposition becomes less and less, and the colour of the solution varies from yellow, green, and blue, and is at length colourless. These changes may be witnessed, not only by adding successive quantities of nitrous acid to water, and thereby at length producing a strong nitric acid, but commencing with the latter, saturating it with nitrous acid, and then successively diluting with water.

When nitrous acid is mixed with a very small quantity of water, no binoxide of nitrogen is disengaged, but the liquid becomes green, like the colour of hyponitrous acid. I have repeatedly obtained a similar liquid in preparing nitrous acid from nitrate of lead, when the materials were not adequately dried; and that green liquid, when allowed to dissipate in the air, leaves some nitric aid behind. From these facts it seems probable that in the decomposition of nitrous acid by water, the first change is the conversion of nitrous into nitric and hyponitrous acids, which last is subsequently changed, when the required quantity of water is present, into nitri acid and binoxide of nitrogen. It may thus well happen that hyponitrous acid contributes to produce the varying colours above described.

Some chemists consider nitrous acid as a compound of nitric and hyponitrous acids, rather than of nitrogen and oxygen. In fact, on adding nitrous acid to an alkaline solution, we obtain a nitrate and hyponitrite, a circumstance which has given rise to the notion that nitrous acid cannot act as a distinct acid. Berzelius and Mitscherlich affirm that the salts commonly termed nitrites, such as nitrite of baryta and potassa, made by heating the corresponding nitrates to gentle redness, contain hyponitrous acid.

NITRIC ACID.

If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquirèd acid properties. On neutralizing the solution with potassa, or what is better, by putting a solution of that alkali instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potassa. This experiment was performed in 1785 by Mr. Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot in this way be accurately determined.

Nitric acid may be formed much more conveniently by adding binoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that nitric acid may in this manner be obtained quite free from nitrous or hyponitrous acid; and that it is composed of 100 measures of nitrogen and 250 of oxygen. This result has been confirmed by the experiments of Davy, Henry, Berzelius, and others, fully establishing the composition as already stated.

Nitric acid cannot exist in an insulated state. Binoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen gas without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; a liquid which, in its concentrated state, is the nitric acid of the Pharmacopœia. By manufacturers it is better known by the name of *aqua fortis*.

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of oil of vitriol; and common nitre, as the cheapest of the nitrates, is employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest oil of vitriol is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitric acid vapours, which must be collected in a cool receiver. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and oil of vitriol; and the Edinburgh and Dublin Colleges employ three parts of nitre to two of the acid. In the process of the London College, the alkali of the nitre is left as a bisulphate in the retort; since one equivalent of nitre (54 nitric acid and 47 potassa) is 101, and the nearly equal number 98 corresponds to two equivalents of oil of vitriol, which contain two eq. of anhydrous sulphuric acid and two eq. of water. During the distillation the nitric acid passes over along with one and a half eq. of water, and half an equivalent of water is retained by the bisulphate of potassa. The presence of water is essential: nitric acid of sp. gr. 1.50 consists of real or anhydrous acid and water in the ratio of one eq. to one and a half, or two to three; and unless water in at least this proportion be supplied, a proportional quantity of nitric acid is resolved, at the moment of quitting the potassa, into oxygen and nitrous acid (Phillips, in Phil. Mag. ii. 430). If the mixture be introduced into the retort without soiling its neck, and the heat be cautiously raised, the product will be quite free from sulphuric acid; and, therefore, the second distillation from nitre, recommended in the Pharmacopœia, is superfluous.

The proportions of the Edinburgh and Dublin Colleges are such, that the residual salt is a mixture of sulphate and bisulphate of potassa. The acid of the nitre does not receive from the oil of vitriol the requisite quantity of water, and hence part of it is decomposed, yielding towards the close of the operation an abundant supply of nitrous acid fumes. If the receiver be kept cool, nearly all these vapours are condensed, and the product is a mixture of nitric and nitrous acids, of a deep orange-red colour, very strong and fuming, and of a greater specific gravity, though proportionally less in quantity, than that obtained by the foregoing process. The specific gravity of the pale acid is 1.500; while that of the red acid is 1.520, or by previously drying the nitre and boiling the sulphuric acid, Dr. Hope states that it may be made so high as 1.54.

Some manufacturers decompose nitre with half its weight of sulphuric acid, thus employing the ingredients in the proportion of one equivalent of each. In this case about half of the nitric acid is decomposed, and considerable loss sustained, unless the requisite quantity of water is previously mixed with the sulphuric acid, or water be placed in the receiver to condense the nitrous acid. Some of the nitre is likewise apt to escape decomposition; and the residue, consisting of neutral sulphate, which is much less soluble than the bisulphate, is removed from the retort with difficulty.

In none of the preceding processes, not even in the first, is the product quite colourless; for at the commencement and close of the operation, nitrous acid fumes are disengaged, which communicate a straw-yellow or an orange-red tint, according to their quantity. If a very pale acid is required, two receivers should be used; one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called nitrous acid by the College; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing anhydrous nitrous with colourless nitric acid. It is easy to convert the common mixed acid of the College into colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in most cases for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains portions of sulphuric and hydrochloric acid. The former is derived from the acid which is used in the process; and the latter from sea-salt, which is frequently mixed with nitre. These impurities may be detected by adding a few drops of a solution of chloride of barium and nitrate of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If chloride of barium cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of silver, the presence of hydrochloric acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate hydrochloric acid, it is necessary to drop a solution of nitrate of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Nitric acid possesses acid properties in an eminent degree. A few drops of it diluted with a considerable quantity of water form an acid solution, which reddens litmus paper permanently. It unites with and neutralizes alkaline substances, forming with them salts which are called *nitrates*. In its purest and most concentrated state it is colourless, and has a specific gravity of 1.50 or 1.510. It still contains a considerable quantity of water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of density 1.50 contains 20 per cent. of water, according to the experiments of Mr. Phillips, and 20.3 per cent. according to those of Dr. Ure.* Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its density is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. Dr. Ure found that when 58 measures of nitric acid of density 1.5 are suddenly mixed with 42 of water, the temperature rises from 60 to 140° F.; and the mixture, on cooling to 60°, occupies the space of 92.65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and if the mixture is made in due proportion, intense cold will be generated. (Page 39.)

Nitric acid boils at 248° F., and may be distilled without suffering material change. An acid of lower density than 1.42 becomes stronger by being heated, because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1.42 is weakened by the application of heat.

Nitric acid may be frozen by cold. The temperature at which congelation takes place, varies with the strength of the acid. The strongest acid freezes at about 50° below zero. When diluted with half its weight of water, it becomes solid at —1½° F. By the addition of a little more water, its freezing point is lowered to —45° F.

Nitric acid acts powerfully on substances which are disposed to unite with oxygen; and hence it is much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into *acids by* its action. All vegetable substances are decomposed *by* it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the former, and carbonic acid with the latter. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity it acts as a powerful cautery, destroying the organization of the part entirely.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into binoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen, is disengaged at the same time. The escape of nitrous acid in these cases seems owing, according to some late observations of Mr. Phillips, not so much to its direct formation, but to the binoxide at first formed acting on the nitric acid of the solution. Direct solar light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former escapes as gas; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is transmitted through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

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* See his table in the Appendix, showing the strength of diluted acid of different densities.

Nitric acid may also be deoxidized by transmitting a current of binoxide of nitrogen through it. That gas, by taking oxygen from the nitric, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived from two sources, gives a colour to the nitric acid, the depth and kind of which depend on the strength of the acid. On saturating with binoxide of nitrogen four separate portions of nitric acid of the densities 1.15, 1.35, 1.40, and 1.50, the colour will be blue in the first, green in the second, yellow in the third, and brownish-red in the fourth; and acid of 1.05 is not coloured at all. Mr. Phillips found that acid of density 1.497 acquired a density 1.541, that is, was made stronger, by saturation with the binoxide: but those acids which become green are much weakened, because nitrous acid, formed at the expense of the nitric acid, is decomposed by the water of the solution.

All the salts of nitric acid are soluble in water, and, therefore, it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, emitting ruddy fumes of nitrous acid, and by its forming with potassa a neutral salt, which crystallizes in prisms, and has all the properties of nitre. Gold-leaf is a still more delicate test. When hydrochloric acid is added to the solution of a nitrate, chlorine is disengaged, and the liquid hence acquires the property of dissolving gold-leaf; but as the action of hydrochloric acid on the salts of chloric, bromic, iodic, and selenic acids likewise yields a solution capable of dissolving gold, no inference can be drawn from the experiment, unless the absence of these acids shall have been previously demonstrated. Another character which may be useful is to mix the supposed nitric acid or nitrate with dilute sulphuric acid in a tube, add a few fragments of pure zinc, and set fire to the hydrogen as it issues: if nitric acid be present, the flame of the hydrogen will have a greenish-white tint, due to admixture with binoxide of nitrogen. This test occurred to my assistant, Mr. Belmain, and Mr. Maitland at the same time proposed alcohol instead of zinc with the same intention. A very delicate test has been proposed by Dr. O'Shaugnessy, founded on the orange-red followed by a yellow colour, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. (Lancet, 1829–30.) It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid.

SECTION VI.

CARBON.

When wood is heated to a certain degree in the open air, it takes fire, and burns with the formation of water and carbonic acid gas till the whole of it is consumed. A small portion of ashes, consisting of the alkaline and earthy matters which had formed a part of the wood, is the sole residue. But if the wood be heated to redness in close vessels, so that atmospheric air cannot have free access to it, a large quantity of gaseous and other volatile matters is expelled, and a black, hard, porous substance is left, called *charcoal.*

Charcoal may be procured from other sources. When the volatile matters are driven off from coal, as in the process for making coal gas, a peculiar kind of charcoal, called *coke*, remains in the retort. Most animal and vegetable substances yield it when ignited in close vessels. Thus, a very pure charcoal may be procured from starch or sugar; and from the oil of turpentine or spirit of wine, by passing their vapour through tubes heated to redness. When bones are made red-hot in a covered crucible, a black mass remains, which consists of charcoal mixed with the earthy matters of the bone. It is called *ivory black*, or *animal charcoal.*

Charcoal is hard and brittle, conducts heat very slowly, but is a good conductor of electricity. It is quite insoluble in water, is attacked with difficulty by nitric acid, and is little effected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

Charcoal possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from box-wood absorbs, during the space of 24 or 36 hours, of

Ammoniacal gas	90 times its volume.
Muriatic acid	85
Sulphurous acid	65
Sulphuretted hydrogen	55
Nitrous oxide	40
Carbonic acid	35
Olefiant gas	35
Carbonic oxide	9.42
Oxygen	9.25
Nitrogen	7.5
Hydrogen	1.75

The absorbing power of charcoal, with respect to gases, cannot be attributed to chemical action; for the quantity of each gas, which is absorbed, bears no relation whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

The porous texture of charcoal accounts for the fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Messrs. Allen and Pepys determined experimentally the increase in weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent; that from *lignum vitæ*, 9.6; that from box, 14; from beech, 16.3; from oak, 16.5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the charcoal retains with such force, that it cannot be completely separated from them without exposure to a red heat. Vogel has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way. (Schweigger's Journal, iv.)

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly if not quite colourless. Tainted flesh may be deprived of its odour by this means, and foul water be purified by filtration through charcoal. The substance commonly employed to decolorize fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

The pure inflammable principle, which is the characteristic ingredient of all kinds of charcoal, is called *carbon*. In coke it is in a very impure form. Wood-charcoal contains about 1-50th of its weight of alkaline and earthy salts, which constitute the ashes when this species of charcoal is burned. In plumbago, the carbon is thought to be combined with a small portion of metallic iron. Charcoal derived from spirit of wine is almost quite pure; and the diamond is carbon in a state of absolute purity.

The diamond is the hardest substance in nature. Its texture is crystalline in a high degree, and its cleavage very perfect. Its primary form is the octohedron. Its specific gravity is 3.520. Acids and alkalies do not act upon it; and it bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to redness in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments of the Florentine academicians in 1694, and subsequently confirmed by several philosophers. Lavoisier first proved it to contain carbon by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube; and comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion, that charcoal and the diamond are chemically the same substance; and that the difference in their physical character is solely dependent on a difference of aggregation.* This conclusion was confirmed by the experiments of Allen and Pepys,† and Davy,‡ who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen; but its quantity is so small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained by charcoal with such force, that it cannot be expelled by the temperature of ignition.

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* Philos. Trans. for 1797. † Ibid. 1807. ‡ Ibid. 1814.

Chemists are agreed that carbonic acid is a compound of one equivalent of carbon and two equivalents of oxygen, and that carbonic acid gas contains its own volume of oxygen. Hence the difference of the densities of carbonic acid and oxygen (1.5239—1.1024), or 0.4215 is the quantity of carbon united with 1.1024 of oxygen, being the ratio of 6.12 to 16. Dr. Thomson, on the same principles but different facts, considers 6 as the true equivalent; but the composition of vegetable compounds attests that 6.12 is more nearly correct than 6, though the latter is often a sufficient approximation. The hypothetical density of the vapour of carbon, calculated as explained at page 147, is 0.4215, and 100 cubic inches of it should weigh 13.0714 grains.

The composition of the compounds of carbon described in this section is as follows:—

	Carbon.		Oxygen.		Equiv.	Formulæ.
Carbonic oxide	6.12 or 1 eq.	+	8 or 1 eq.	=	14.12	$C + O$ or $\dot{C}$.
Carbonic acid	6.12 or 1 eq.	+	16 or 2 eq.	=	22.12	$C + 2O$ or $\ddot{C}$.

Carbonic oxide gas is theoretically considered as a compound of 100 measures of the vapour of carbon and 50 of oxygen condensed into 100 measures; and carbonic acid gas, of 100 measures of the vapour of carbon and 100 of oxygen condensed into 100 measures.

CARBONIC ACID.

Carbonic acid was discovered by Dr. Black in 1757, and described by him in his inaugural dissertation on magnesia under the name of *fixed air*. He observed the existence of this gas in common limestone and magnesia, and found that it may be expelled from these substances by the action of heat or acids. He also remarked that the same gas is formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The same experiment has been repeated by Davy, Allen and Pepys, and others, with the result that in the combustion of diamond or other pure carbonaceous matter, the oxygen undergoes no change of volume, or in other words that carbonic acid gas contains its own volume of oxygen. Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or carbonate of lime heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Carbonic acid is most conveniently prepared for the purposes of experiment by the action of hydrochloric acid, diluted with two or three times its weight of water, on fragments of marble, when the hydrochloric acid takes the lime, and carbonic acid gas escapes with effervescence.

Carbonic acid, as thus procured, is a colourless, inodorous, elastic fluid, which possesses all the physical characters of the gases in an eminent degree, and requires a pressure of thirty-six atmospheres to condense it into a liquid. The exact knowledge of its density is still an important desideratum: it is estimated at 1.524 by Dulong and Berzelius, and at 1.5277 by Dr. Thomson. (First Principles, i. 143.) According to the estimate of the former, which I have adopted, 100 cubic inches should weigh 47.26 grains.

Carbonic acid extinguishes burning substances of all kinds, and the combustion does not cease from the want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air and one of carbonic acid.

It is not better qualified to support the respiration of animals; for its presence, even in moderate proportion, is soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. If the light is extinguished, the air is certainly impure; and there is generally thought to be no danger, if the candle continues to burn. But some instances have been known of the atmosphere being sufficiently loaded with carbonic acid to produce insensibility, and yet not so impure as to extinguish a burning candle. (Christison on Poisons, 2nd Ed. 707.) When an attempt is made to inspire pure carbonic acid, violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

Carbonic acid is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime-water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime-water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Carbonic acid is absorbed by water. This may easily be demonstrated by agitating the gas with that liquid, or by leaving a jar full of it inverted over water. In the first case the gas disappears in the course of a minute; and in the latter it is gradually absorbed. Recently boiled water dissolves its own volume of carbonic acid at the common temperature and pressure; but it will take up much more if the pressure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume when the pressure is trebled.

A saturated solution of carbonic acid may be made by transmitting a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nooth's apparatus, so as to aid the absorption by pressure. Water and other liquids which have been charged with carbonic acid under great pressure, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cider, or brisk champaign, is owing to the escape of carbonic acid gas. Water, which is fully saturated with carbonic acid gas, sparkles when it is poured from one vessel into another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime-water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime-water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale, is in a great measure owing to the presence of carbonic acid; by the loss of which, on exposure to the air, they become stale. All kinds of spring and well-water contain carbonic acid absorbed from the atmosphere, and to which they are partly indebted for their pleasant flavour. Boiled water has an insipid taste from the absence of carbonic acid.

Carbonic acid is always present in the atmosphere, even at the summit

of the highest mountains, or at a distance of several thousand feet abo
ground. Its presence may be demonstrated by exposing lime-water
open vessel to the air, when its surface will soon be covered with a p
which is carbonate of lime. The origin of the carbonic acid is o
Besides being formed abundantly by the combustion of all substances
contain carbon, the respiration of animals is a fruitful source of it, as n
proved by breathing for a few minutes into lime-water; and it is also gen
in all the spontaneous changes to which dead animal and vegetable m
are subject. The carbonic acid proceeding from such sources, is com
diffused equably through the air; but when any of these processes oc
low confined situations, as at the bottom of old wells, the gas is then
accumulate there, and form an atmosphere called *choke damp*, which i
to any animals that are placed in it. These accumulations happily
take place, except when there is some local origin for the carbonic ac
for example, when it is generated by fermentative processes going on
surface of the ground, or when it issues directly from the earth, as ha
at the Grotto del Cane in Italy, and at Pyrmont in Westphalia. Th
no real foundation for the opinion that carbonic acid can separate itself
the great mass of the atmosphere, and accumulate in a low situation m
by the force of gravity. Such a supposition is contrary to the well-k
tendency of gases to diffuse themselves equally through each other.
also contradicted by observation; for many deep pits, which are free
putrefying organic remains, though otherwise favourably situated fo
accumulations, contain pure atmospheric air.

Though carbonic acid is the product of many natural operations, che
have not hitherto noticed any increase in the quantity contained i
atmosphere. The only known process which tends to prevent increa
its proportion, is that of vegetation. Growing plants purify the a
withdrawing carbonic acid, and yielding an equal volume of pure oxyg
return; but whether a full compensation is produced by this cause, ha
yet been satisfactorily determined.

Carbonic acid is contained in the earth. Many mineral springs, su
those of Tunbridge, Pyrmont, and Carlsbad, are highly charged wi
In combination with lime it forms extensive masses of rock, which g
gists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so consti
are called *carbonates*. Its acid properties are feeble, so that it is una
neutralize completely the alkaline properties of potassa, soda, and
For the same reason, all the carbonates, without exception, are decom
by the hydrochloric and all the stronger acids, when carbonic acid
placed, and escapes in the form of gas.

CARBONIC OXIDE GAS.

When two parts of well-dried chalk and one of pure iron filings a
ed together, and exposed in a gun barrel to a red heat, a large qua
aëriform matter is evolved, which may be collected over water. On
nation, it is found to contain two compounds of carbon and oxygen
which is carbonic acid, and the other *carbonic oxide*. By wash
mixed gases with lime-water, the carbonic acid is absorbed, and
oxide gas is left in a state of purity. A very elegant mode of p
carbonic oxide has been suggested by Dumas. (Ed. Journal of Sci
350.) The process consists in mixing binoxalate of potassa with fi
times its weight of concentrated sulphuric acid, and heating the m
a retort or other convenient glass vessel. Effervescence soon ensu
to the escape of gas, consisting of equal measures of carbonic acid
bonic oxide gases; and on absorbing the former by an alkaline sol
latter is left in a state of perfect purity. To comprehend the theo
process it is necessary to premise, that oxalic acid is a compoun
measures of carbonic acid and carbonic oxide, or at least its eleme

the proportion to form these gases; and that it cannot exist unless in combination with water or some other substance. Now the sulphuric acid unites both with the potassa and water of the binoxalate, and the oxalic acid being thus set free, is instantly decomposed. Oxalic acid may be substituted in this process for binoxalate of potassa.

Priestley discovered this gas by igniting chalk in a gun-barrel, and afterwards obtained it in greater quantity from chalk and iron filings. He supposed it to be a mixture of hydrogen and carbonic acid gases. Its real nature was pointed out by Mr. Cruickshank,* and about the same time by Clément and Désormes.†

Carbonic oxide gas is colourless and insipid. It does not affect the blue colour of vegetables in any way; nor does it combine, like carbonic acid, with lime or any of the pure alkalies. It is very sparingly dissolved by water. Lime-water does not absorb it, nor is its transparency affected by it.

Carbonic oxide is inflammable. When a lighted taper is plunged into a jar full of that gas, the taper is extinguished; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid, a fact which proves that it does not contain any hydrogen.

Carbonic oxide gas cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headach and other unpleasant feelings; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If they are mixed together in the ratio of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's eudiometer by electricity, so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappears, and 100 measures of carbonic acid gas occupy their place. From this fact, first ascertained by Berthollet, and since confirmed by subsequent observation, it follows that carbonic oxide contains half as much oxygen, and as much carbon, as carbonic acid. Accordingly its density should be 0.4215 (sp. gr. of carbon vapour) +0.5512 (half the sp. gr. of oxygen gas) =0.9727, which is the number found experimentally by Dulong and Berzelius. Hence 100 cubic inches should weigh 30.1650 grains.

The first process mentioned for generating carbonic oxide will now be intelligible. The principle of the method is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonate of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or charcoal. The carbonate is reduced to the caustic state, and its carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or charcoal. When the former is used, oxide of iron is the product; when charcoal is employed, the charcoal itself is oxidized, and yields carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, and copper are the cheapest and most convenient. It may also be formed by transmitting a current of carbonic acid gas over ignited charcoal. In all these processes, it is essential that the ingredients be quite free from moisture and hydrogen, otherwise some carburetted hydrogen gas would be generated. The product should always be washed with lime-water to separate it from carbonic acid.

Dr. Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one-half of its oxygen to the former; water is generated, and carbonic oxide produced. On electrifying a mixture of equal measures of carbonic oxide and protoxide of nitrogen, both gases are decomposed without change of volume, and the residue consists of equal measures of carbonic acid and nitrogen gases. The carbonic oxide should be in very slight excess, in order to ensure the success of the experiment. On this fact is founded Dr. Henry's method of analyzing protoxide of nitrogen, and testing its purity, as will be more particularly mentioned in the fourth part of the work.

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* Nicholson's Journal, 4to. Ed. vol. v. † Annales de Chimie, vol. xxxix.

SECTION VII.

SULPHUR.

Sulphur occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but it is sometimes met with crystallized in the form of an oblique rhombic octohedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing iron pyrites to a red heat in close vessels.

Sulphur is a brittle solid of a greenish-yellow colour, emits a peculiar odour when rubbed, and has little taste. It is a non-conductor of electricity, and is excited negatively by friction. Its specific gravity is 1.99. Its point of fusion is 216° F; between 230° and 280° it possesses the highest degree of fluidity, is then of an amber colour, and if cast into cylindrical moulds, forms the common roll sulphur of commerce. It begins to thicken near 320°, and acquires a reddish tint; and at temperatures between 428° and 482°, it is so tenacious that the vessel may be inverted without causing it to change its place. From 482° to its boiling point it again becomes liquid, but never to the same extent as when at 248°. When heated to at least 428°, and then poured into water, it becomes a ductile mass, which may be used for taking the impression of seals. (Dumas.)

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of common roll sulphur; and by good management regular crystals may be obtained. For this purpose several pounds of sulphur should be melted in an earthen crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour even before it is completely fused. At 550° or 600° F. it volatilizes rapidly, and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of detached crystalline grains, called *flowers of sulphur*. In this state however, it is not quite pure; for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

The density of sulphur vapour was found by Dumas to lie between 6.51 and 6.617, and by Mitscherlich to be 6.9 (An. de Ch. et de Ph. lv. 8.): its density by calculation (page 146) is 6.6558. Hence, could the vapour continue as such at 60° F. and 30 Bar., 100 cubic inches should weigh 206.4076 grains.

Sulphur is insoluble in water, but unites with it under favourable circumstances, forming the white *hydrate of sulphur*,* termed *lac sulphuris*. It dissolves readily in boiling oil of turpentine. The solution has a reddish-brown colour like melted sulphur, and if fully saturated deposites numerous small crystals in cooling. Sulphur is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Sir H. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some hydrosulphuric acid gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as in no wise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger, and of a bluish-white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture be present.

The oxygen in the oxide and acid of neutral sulphates is in the ratio of 1 to 3; so that when the composition of a metallic oxide, and the quantity of acid by which it is neutralized are known, the equivalent of sulphur may be calculated. On this principle has Berzelius inferred, from the composition of sulphate of the oxide of lead, that the equivalent of sulphur is 16.12; and the number which I have obtained in the same way from the same salt and from sulphate of baryta, is 16.09. As a mean of these results, 16.1 may be taken as the equivalent of sulphur. The number 16, adopted in this country, is, therefore, for many purposes a sufficient approximation.

The compounds of sulphur described in this section are composed as follows:—

	Sulphur.		Oxygen.		Equiv.	Formulæ.
Sulphurous acid	16.1 or 1 eq.	+	16 or 2 eq.	=	32.1	$S+2O$ or $\ddot{S}$
Sulphuric acid	16.1 or 1 eq.	+	24 or 3 eq.	=	40.1	$S+3O$ or $\dddot{S}$
Hyposulphurous acid	32.2 or 2 eq.	+	16 or 2 eq.	=	48.2	$2S+2O$ or $\underline{\ddot{S}}$
Hyposulphuric acid	32.2 or 2 eq.	+	40 or 5 eq.	=	72.2	$2S+5O$ or $\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{S}}$

Taking 16.66 as the combining volume of the vapour of sulphur, the weight of which is represented by 1.1093 (page 149), these compounds by measure are thus constituted:—

	Sulph.		Oxy.	Cond. into.	Densities.
Sulphurous acid	16.66	+	100	100	1.1093+1.1024=2.2117
Sulphuric acid	16.66	+	150	100	1.1093+1.6536=2.7629
Hyposulphurous acid	33.33	+	100	unknown.	
Hyposulphuric acid	33.33	+	250	unknown.	

SULPHUROUS ACID GAS.

Pure sulphurous acid, at the common temperature and pressure, is a colourless transparent gas, which was first obtained in a separate state by Priestley. It is the sole product when sulphur is burned in air or dry oxygen gas, and is the cause of the peculiar odour emitted by that substance during its combustion. It may also be prepared by depriving sulphuric acid of one equivalent of its oxygen, which may be done in several ways. If chips of wood, straw, cork, oil, or other vegetable matters, be heated in strong sulphuric acid, the carbon and hydrogen of those substances deprive the acid of part of its oxygen, and convert it into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect. One portion of sulphuric acid yields oxygen to the metal, and is thereby converted into sulphurous acid; while the metallic oxide, at the moment of its formation, unites with some of the undecomposed sulphuric acid. The best method of obtaining pure sulphurous acid gas, is by putting two parts of mercury and three of sulphuric acid into a glass retort, the beak of which is received under mercury, and heating the mixture by an Argand lamp. Effervescence soon takes place, a large quantity of pure sulphurous acid is disengaged, and sulphate of an oxide of mercury remains in the retort.

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* Berzelius asserts, that the lac sulphuris is not a hydrate, but sulphur united with a minute portion of hydrogen.—*Ed.*

Sulphurous acid gas is distinguished from all other gaseous fluids by its suffocating pungent odour. All burning bodies, when immersed in it, are extinguished without setting fire to the gas itself. It is fatal to all animals which are placed in it. A violent spasm of the glottis takes place, by which the entrance of the gas into the lungs is prevented; and even when diluted with air, it excites cough, and causes a peculiar uneasiness about the chest.

Recently boiled water dissolves about 33 times its volume of sulphurous acid at 60° F. and 30 inches of the barometer, forming a solution which has the peculiar odour of that compound, and from which the gas, unchanged in its properties, may be expelled by ebullition.

Sulphurous acid has considerable bleaching properties. It reddens litmus paper, and then slowly bleaches it. Most vegetable colouring matters, such as those of the rose and violet, are speedily removed, without being first reddened. It is remarkable that the colouring principle is not destroyed; for it may be restored either by a stronger acid or by an alkali.

Sir H. Davy inferred from his experiments on the combustion of sulphur in dry oxygen gas, (Elements, p. 273,) that the volume of the oxygen is not altered during the process, or that sulphurous acid gas contains its own volume of oxygen, a conclusion which is now admitted; and, therefore, the difference in the densities of these gases gives the quantity of combined sulphur. Adopting 2.2117 as the density of sulphurous acid gas, then 2.2117—1.1024 (sp. gr. of oxygen) = 1.1093 as the sulphur combined with 1.1024 of oxygen; now 1.1024 is to 1.1093 as 16 to 16.1, being the composition already given. I have in fact selected 2.2117 as the density of sulphurous acid gas on account of this coincidence, seeing that the density as found by experiment cannot be relied on: Berzelius makes it 2.247, and Thomson 2.222, both of which are too high, if the density of oxygen is 1.1024. Agreeably to this view 100 cubic inches of sulphurous acid gas should weigh 68.5885 grains.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without chemical action. But if a little water be admitted, the sulphurous acid gradually unites with oxygen, and sulphuric acid is generated. The facility with which this change ensues is such, that a solution of sulphurous acid in water cannot be preserved, except atmospheric air be carefully excluded. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. When mixed with peroxide of iron in solution, it gradually deprives that compound of part of its oxygen, and converts it into the protoxide. The solutions of metals which have a weak affinity for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid by yielding some of its oxygen. Peroxide of manganese causes a similar change, and is itself converted into protoxide of manganese, which unites with the resulting sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Of all the gases, sulphurous acid is most readily liquefied by compression. According to Mr. Faraday, it is condensed by a force equal to the pressure of two atmospheres. M. Bussy (Annals of Phil. viii. 307, N. S.) has obtained it in a liquid form under the usual atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of snow and salt. The anhydrous liquid acid has a density of 1.45. It boils at 14° F.; and from the rapidity of its evaporation at common temperatures, it may be used advantageously for producing intense cold. Bussy succeeded in freezing mercury, and liquefying several of the gases, by the cold produced during its evaporation. De la Rive states it to be a non-conductor of electricity; but Mr. Kemp, of Edinburgh, found it to be a good conductor. The former adds, also, that when exposed to cold in the moist state, a crystalline solid hydrate is formed, which contains 20 per cent of water, and probably consists of one equivalent of the acid to one of water.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*, which are decomposed by sulphuric acid, and then emit the characteristic odour of sulphurous acid.

SULPHURIC ACID.

Sulphuric acid, or *oil of vitriol* as it is often called, was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. One of these has been long pursued in the manufactory at Nordhausen in Germany, and consists in decomposing protosulphate of iron (green vitriol) by heat. This salt contains six equivalents of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Dr. Thomson, contains one equivalent of water. On exposing this dried protosulphate to a red heat, its acid is wholly expelled, the greater part passing over unchanged into the receiver, in combination with the water of the salt. Part of the acid, however, is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, since, in the beginning of the distillation, it unites with the protoxide of iron. Peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily liquid of a brownish tint. It emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid*. Its specific gravity is stated at 1.896 and 1.90. According to Dr. Thomson it consists of 80 parts or two equivalents of anhydrous acid, and 9 parts or one equivalent of water.

On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and heating it gently, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is shown by the experiments of Thomson, Ure, and Bussy, to be pure anhydrous sulphuric acid. It is tough and elastic; liquefies at 66° F. and boils at a temperature between 104° and 122°, forming, if no moisture is present, a transparent vapour. Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The other process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur previously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air, which supports the combustion, conducts the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitric acid, in losing oxygen, is converted, partly perhaps into nitrous acid, but chiefly, I apprehend, into binoxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances, present in the leaden chamber, are, therefore, sulphurous and nitrous acids, atmospheric air, and watery vapour. The explanation of the mode in which these substances react on each other, so as to form sulphuric acid, was suggested by the experiments of Clément and Désormes, (An. de Ch. lix.) and Sir H. Davy, (Elements, p. 276.) When dry sulphurous acid gas and nitrous vapour are mixed together in a glass vessel quite free from moisture, no change ensues; but if a few drops of water be added, in order to fill the space with aqueous vapour, the white crystalline compound, described at page 179 is immediately produced. Clément and Désormes believed it to consist of sulphuric acid, binoxide of nitrogen, and water; and Davy, of sulphurous acid, nitrous acid, and water. But the observation, that the same compound might be made with sulphuric and anhydrous nitrous acids, and that when decomposed by water, both nitrous acid and binoxide of nitrogen are disengaged, led Gay-Lussac to the opinion which now seems to be fully substantiated by experiment. (Page 179.) A consistent account may, therefore, be given of what really takes place within the leaden chambers.—The mutual reaction of humidity, sulphurous acid, and nitrous acid, gives rise to the crystalline compound of sulphuric acid, hyponitrous acid, and water; and when this solid falls into the water of the chamber, it is instantly decomposed, sulphuric acid is dissolved, and nitrous acid and binoxide of nitrogen escape with effervescence. The nitrous acid thus set free, as well as that reproduced by the binoxide uniting with the oxygen of the atmosphere, is again intermixed with sulphurous acid and humidity, and thus gives rise to a second portion of the crystalline solid, which undergoes the same change as the first. A certain portion of nitric acid is usually formed by the action of water on the nitrous acid; but the presence of sulphuric acid in that water tends to prevent the free decomposition of nitrous acid which pure water produces. When the water of the chamber by these successive combinations and decompositions is sufficiently charged with acid, it is drawn off, and concentrated by evaporation. During this process, if carried far enough, the nitric acid formed in the leaden chamber is expelled. From the foregoing account it consequently appears that the oxygen, by which the sulphurous is converted into sulphuric acid, is in reality supplied by the air; that the combination is effected, not directly, but through the medium of nitrous acid; and that a small quantity of nitrous acid is sufficient for the production of a large quantity of sulphuric acid. The decomposition of the crystalline solid by water seems owing to the strong affinity of that liquid for sulphuric acid.

Sulphuric acid, as thus prepared, is never quite pure. It contains some sulphate of potassa and of lead, the former derived from the nitre employed in making it, and the latter from the leaden chamber. To separate these impurities, the acid should be distilled from a glass or platinum retort. The former may be used with safety by putting into it some fragments of platinum leaf, which cause the acid to boil freely on the application of heat, without danger of breaking the vessel.

Pure sulphuric acid, as obtained by the second process, is a dense, colourless, oily fluid, which boils at 620° F., and has a specific gravity, in its most concentrated form, of 1.847 or a little higher, never exceeding 1.850. Mitscherlich found the density of its vapour to be 3; but the calculated number, 2.7629, is probably nearer the truth. It is one of the strongest acids with which chemists are acquainted, and when undiluted is powerfully corrosive, It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalies.

Sulphuric acid in a very concentrated state dissolves small quantities of sulphur, and acquires a blue, green, or brown tint. Tellurium and selenium are also sparingly dissolved, the former causing a crimson, and the latter a green colour. By dilution with water, these substances subside unchanged; but if heat is applied, they are oxidized at the expense of the acid, and sulphurous acid gas is disengaged. Charcoal also appears soluble to a small extent in sulphuric acid, communicating at first a pink, and then a dark reddish-brown tint.

Sulphuric acid has a very great affinity for water, and unites with it in every proportion. The combination takes place with production of intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Dr. Ure, to 300° F. By its attraction for water, it causes the sudden liquefaction of snow; and if mixed with it in due proportion (p. 39), intense cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. The action of sulphuric acid in destroying the texture of the skin, in forming ethers, and in decomposing animal and vegetable substances in general, seems dependent on its affinity for water.

It is frequently important to know the quantity of real acid contained in liquid sulphuric acid of different strengths. When great accuracy is requisite, this information should always be ascertained by neutralizing a specimen of the acid with an alkali. For this purpose, dilute a known weight of the acid moderately with water, and, while warm, add pure anhydrous carbonate of soda, until the solution is exactly neutral. Every 53.42 parts of carbonate of soda, required to produce this effect, correspond to 40.1 parts of real sulphuric acid. But if minute precision is not desired, the strength of the acid may be estimated by its specific gravity, according to the table of Dr. Ure inserted in the Appendix.

Sulphuric acid of commerce freezes at — 15° F. Diluted with water so as to have a specific gravity of 1.78 it congeals even above 32°, and remains in the solid state, according to Mr. Keir, till the temperature rises to 45°. When mixed with rather more than its weight of water, its freezing point is lowered to —36° F.

The composition of sulphuric acid as before given is founded on the observation of Gay-Lussac, that when the vapour of sulphuric acid is passed through a small porcelain tube heated to redness, it is resolved into two measures of sulphurous acid gas and one of oxygen. Berzelius has confirmed this conclusion by directly converting a known weight of sulphur into sulphuric acid.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of chloride of barium is added to a liquid containing sulphuric acid, it causes a white precipitate, sulphate of baryta, which is characterized by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

Hyposulphurous Acid.—This acid may be formed either by digesting sulphur in a solution of any sulphite, or by transmitting a current of sulphurous acid into a solution of sulphuret of calcium or strontium. In the former case, the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; and in the latter, the sulphurous acid gives part of its oxygen to the metal, and its remaining oxygen unites with sulphur. Three equivalents of sulphurous acid and two of sulphuret of calcium contain the elements for forming two equivalents of hyposulphite of lime, one eq. of sulphur being deposited. A convenient solution for this purpose is made by boiling 3 parts of slaked lime and 1 of sulphur with 20 parts of water for one hour, and decanting the clear liquid from the undissolved portions; but when this solution is used, the deposite of sulphur is abundant. Sir J. Herschel states that hyposulphurous acid may be formed by the action of sulphurous acid on iron filings; but the nature of the change is not well understood.

The salts of hyposulphurous acid were first described by Gay-Lussac in the 85th volume of the *Annales de Chimie*, under the name of *sulphuretted sulphites*. Dr. Thomson in his System of Chemistry suggested that the acid of these salts might be regarded as a compound of one equivalent of sulphur and one of oxygen, and proposed for it the name of *hyposulphurous* acid; and the subsequent researches of Sir J. Herschel (Edinburgh Philos. Journal, i. 8 and 396) accorded so entirely with this opinion, that it was universally adopted. But it appears from the experiments of Rose, that though the ratio of its elements is as 16 to 8, the equivalent of the acid, or the quantity required to neutralize one equivalent of an alkali, is not 24 but 48; and hence that its smallest molecule must be formed of two atoms of sulphur united with two atoms of oxygen. (Poggendorff's Ann. xxi. 431.)

Hyposulphurous acid cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as sulphuric or hydrochloric, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Sir J. Herschel succeeded in obtaining free hyposulphurous acid, by adding a slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat. Most of the hyposulphites are soluble in water, and have a bitter taste. The solution precipitates the nitrates of the oxides of silver and mercury black, as sulphuret of the metals; and salts of baryta and oxide of lead are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with hydrochloric acid. The solution of all the neutral hyposulphites has the peculiar property of dissolving recently precipitated chloride of silver in large quantity, and forming with it a liquid of an exceedingly sweet taste.

Hyposulphuric Acid.—This acid was discovered in 1819 by Welter and Gay-Lussac. (An. de Ch. et de Ph. x.) It is formed by transmitting a current of sulphurous acid gas through water containing peroxide of manganese in fine powder; when by a new arrangement of their elements,

2 eq. Sulph. acid & 1 eq. Perox. mang. yield 1 eq. Protox. mang. & 1 eq. Hyposulp. acid.

$$2(S+2O) \qquad Mn+2O \qquad\qquad Mn+O \qquad 2S+5O,$$

hyposulphate of protoxide of manganese remaining in solution. During the action heat is freely evolved, and in consequence sulphuric acid is also generated; but if the peroxide of manganese be pure and the materials kept cool, the formation of sulphuric acid is almost completely prevented. To the liquid, after filtration, a solution of pure baryta or sulphuret of barium in slight excess is added, whereby the manganese is thrown down as an oxide or sulphuret, sulphuric acid as sulphate of baryta, and a solution of hyposulphate of baryta is obtained: the excess of baryta is got rid of by a free current of carbonic acid gas, and then heating the solution. The hyposulphate of baryta crystallizes by evaporation, and on decomposing a solution of that salt by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, the hyposulphuric acid is left in solution.

This compound reddens litmus paper, has a sour taste, and forms neutral salts with the alkalies. It has no odour, by which circumstance it is distinguished from sulphurous acid. It cannot be confounded with sulphuric acid; for it forms soluble salts with baryta, strontia, lime, and oxide of lead, whereas the compounds which sulphuric acid forms with those bases are all insoluble. Hyposulphuric acid cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air-pump, may be concentrated till it has a density of 1.347; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed hyposulphuric acid by exposing neutral hyposulphate of baryta to heat. At a temperature a little above 212° this salt suffers complete decomposition; sulphurous acid gas is disengaged, and neutral sulphate of baryta is obtained. It was thus ascertained that 72 grains of hyposulphuric acid yield 32 grains of sulphurous, and 40 of sulphuric acid; from which it is inferred that hyposulphuric acid is composed either of an equivalent of each of those acids combined with each other, or of two equivalents of sulphur and five of oxygen.

SECTION VIII.

PHOSPHORUS.

Phosphorus (φωσφόρος from φῶς *light* and φέρειν *to carry*), so called from its property of shining in the dark, was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele afterwards described a method of obtaining it from bones, which is now generally practised. The bones are first ignited in an open fire till they become white, so as to destroy their animal matter, and burn away the charcoal derived from it, in which state they contain nearly 4-5ths of phosphate of lime. They are then reduced to a fine powder, and digested for a day or two with half their weight of strong sulphuric acid, with the addition of so much water as will give the consistence of a thin paste. Decomposition of the phosphate of lime is thus effected, and two new salts formed, the sparingly soluble sulphate and a soluble superphosphate of lime. The latter is then dissolved in warm water, and the solution, after being separated by filtration from the sulphate of lime, is evaporated to the consistence of syrup, mixed with a fourth of its weight of powdered charcoal, and strongly heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as its vapour passes over, is condensed. When first obtained it is usually of a reddish-brown colour, owing to the presence of phosphuret of carbon formed during the process. It may be purified by fusion in hot water, and being pressed while liquid through chamois leather, or by a second distillation.

In this process the oxygen of that part of the phosphoric acid which constituted the superphosphate, unites with charcoal, giving rise to carbonic acid and carbonic oxide gases; and phosphate of lime in the state of bone earth, together with redundant charcoal, remains in the retort. The lime acts an important part in fixing the phosphoric acid, which, if not so combined, would distil over before the heat was high enough for its decomposition. In extracting phosphorus from urine, the phosphoric acid should be thrown down by acetate of the oxide of lead; the phosphate of that oxide is then decomposed by charcoal as in the former process. It should be converted by the action of sulphuric acid into a superphosphate of the oxide of lead before admixture with charcoal.

Pure phosphorus is transparent and almost colourless. It is so soft that it may be cut with a knife, and the cut surface has a waxy lustre. At the temperature of 108° it fuses, and at 550° is converted into vapour, which according to Dumas has a density of 4.355. It is soluble by the aid of heat in naphtha, in fixed and volatile oils, in the chloride of sulphur, sulphuret of carbon, and sulphuret of phosphorus. On its cooling from solution in the latter, Mitscherlich obtained it in regular dodecahedral crystals. By the fusion and slow cooling of a large quantity of phosphorus, M. Frantween has obtained very fine crystals of an octohedral form, and as large as a cherry-stone. Thenard has remarked that when phosphorus is fused at 150°, and suddenly cooled by being plunged into cold water, it appears black; but by fusion and slow cooling it recovers its original aspect.

Phosphorus is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes slow combustion, emits a white vapour of a peculiar alliaceous odour, appears distinctly luminous in the dark, and is gradually consumed. On this account, phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shown by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes; and if the temperature of the air is at 60°, the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen gas, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about 80°. But if the oxygen be diluted with nitrogen, hydrogen, or carbonic acid gas, the oxidation occurs at 60°; and it takes place at temperatures still lower in a vessel of pure oxygen, rarefied by diminished pressure.* Mr. Graham finds that the presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus: thus at 66° it is entirely prevented by the presence, (Quart. Jour. of Science, N. S. vi. 83.)

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* If a stick of dry phosphorus be dusted over with powdered resin or sulphur, and then introduced under the receiver of an air-pump, it will be found that, as soon as the exhaustion commences, the phosphorus will become luminous, which appearance increases as the rarefaction proceeds, until finally the phosphorus inflames. Van Bemmelen, who first attempted to account for this phenomenon, attributes it to the combination of the sulphur or resin with the phosphorus, the union of which, accelerated by the influence of the vacuum, gives rise to the evolution of so much heat, as to inflame the phosphorus, or the new compound formed. Berzelius rejects this explanation, as it does not account for an experiment by Van Bemmelen, in which phosphorus was found to take fire under an exhausted receiver, when merely enveloped with cotton. *Berzelius*, *Traité de Chimie*, i. 260.

Professor A. D. Bache, of the University of Pennsylvania, has repeated and extended the experiments of Van Bemmelen, and has had the goodness to communicate to me an abstract of his results. He succeeded in producing the inflammation of the phosphorus, under the circumstances above mentioned, by means of the following substances in a finely divided state, in addition to those employed by Van Bemmelen:—

Carbon in the form of ivory black and wood-charcoal.
Spongy platinum.
Antimony.
Arsenic.
Bisulphuret of mercury.
Sulphuret of antimony.
Silica.
Lime.
Peroxide of manganese.
Hydrate of potassa.
Muriate of ammonia.
Chloride of sodium.
Fluate of lime.
Carbonate of lime.

Sulphur and charcoal were the substances which succeeded most readily. With metallic arsenic there was much difficulty. The temperature of the room has great influence on the success of the experiments.

Professor Bache is of opinion that some of his experiments are unfavourable to the explanation of Van Bemmelen; as for example, those with carbonate of lime and fluor spar, which, though incombustible substances, act with the same energy as sulphur or carbon.—*Ed.*

		Volumes of air.
of 1 volume	of olefiant gas in	450
1 ditto	of vapour of sulphuric ether in	150
1 ditto	of vapour of naphtha in	1820
1 ditto	of vapour of oil of turpentine in	4444,

and by an equally slight impregnation of the vapour of the other essential oils. Their influence is not confined to low temperatures. Phosphorus becomes faintly luminous in the dark, in mixtures of

1 volume of air	and 1 volume	of olefiant gas at	200° F.
1	and 1 ditto	of vapour of ether at	215°
111	and 1 ditto	of vapour of naphtha at	170°
156	and 1 ditto	of vapour of turpentine at	186°

Phosphorus may be sublimed at its boiling temperature, in air containing a considerable proportion of the vapour of oil of turpentine, without diminishing the quantity of oxygen present, provided the heat be gradually and uniformly applied. Mr. Graham has also remarked, that the oxidation of phosphorus in the air is promoted by the presence of hydrochloric acid gas.

A very slight degree of heat is sufficient to inflame phosphorus in the open air. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion, kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionally more vivid.

When phosphorus is kept for a long time under water, especially when exposed to light, its surface acquires a thin coating of white matter, which some have described as an oxide, and others as a hydrate of phosphorus. It seems from some recent experiments by Rose to be neither an oxide nor a hydrate, but phosphorus in a peculiar mechanical state, which deprives it of its usual action upon light and renders it opaque. (Pog. Annalen, xxvii. 565.)

Repeated researches by Berzelius have shown that the oxygen in phosphorous and phosphoric acids is in the ratio of 3 to 5, a result conformable to experiments on the same subject by Dulong, and admitted by most chemists. It is hence inferred that the smallest molecule of phosphoric acid contains five atoms of oxygen. Also Berzelius finds that 31.4 parts of phosphorus require 40 of oxygen for forming phosphoric acid: if this acid consist of one atom of phosphorus and five atoms of oxygen, 31.4 will represent one atom of phosphorus; or if the acid contain two atoms to five, the atom of phosphorus will be half 31.4 or 15.7. It is doubtful which view is preferable, and I, therefore, continue to use 15.7. The combining volume of phosphorus vapour (page 146) is 25.

The compounds of phosphorus described in this section are the following:—

	Phosphorus.	Oxygen.	Equiv.	Formulæ.
Oxide of phosphorus	47.1 or 3 eq. +	8 or 1 eq.	=55.1	3P+O
Hypophosphorous acid	31.4 or 2 eq. +	8 or 1 eq.	=39.4	2P+O or $\dot{P}$
Phosphorous acid	31.4 or 2 eq. +	24 or 3 eq.	=55.4	2P+3O or $\dddot{P}$
Phosphoric acid Pyrophosphoric acid Metaphosphoric acid	31.4 or 2 eq. +	40 or 5 eq.	=71.4	2P+5O or $\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$

COMPOUNDS OF OXYGEN AND PHOSPHORUS.

Oxide.—When a jet of oxygen gas is thrown upon phosphorus while in fusion under hot water, combustion ensues, phosphoric acid is formed, and a number of red particles collect, which have been examined by M. Pelouze, who has shown them to be an oxide of phosphorus. The red matter left when phosphorus is burned is probably of the same nature.

This, the only known oxide of phosphorus, is of a red colour, without taste or odour, and is insoluble in water, ether, alcohol, and oil. It is permanent in the air, even at 662° F., but takes fire at a low red heat. Heated to redness in a tube, phosphorus is expelled, and metaphosphoric acid remains. It takes fire in chlorine gas, and is rapidly oxidized by nitric acid. It does not appear to possess any alkaline character. (An. de Ch. et de Ph. l. 83.)

Hypophosphorous Acid.—This acid was discovered in 1816 by Dulong. (An. de Ch. et de Ph. ii.) When water acts upon the phosphuret of barium the elements of both enter into a new arrangement, giving rise to phosphuretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta. The former escapes in the form of gas, and the two latter combine with the baryta. Hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, hypophosphorous acid is obtained in a free state, and on evaporating the solution, a viscid liquid remains, highly acid and even crystallizable, which is a *hydrate of hypophosphorous acid*. When exposed to heat in close vessels, it undergoes the same kind of change as hydrated phosphorous acid.

Hypophosphorous acid is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potassa, soda, and ammonia dissolve in every proportion in rectified alcohol; and hypophosphite of potassa is even more deliquescent than chloride of calcium. They are all decomposed by heat, and yield the same products as the acid itself. They are conveniently prepared by precipitating hypophosphite of baryta, strontia, or lime, with the alkaline carbonates; or by directly neutralizing these carbonates with hypophosphorous acid. The hypophosphite of baryta, strontia, and lime are formed by boiling these earths in the caustic state in water together with fragments of phosphorus. The same change occurs as during the action of water on phosphuret of barium. The composition of this acid as stated at page 200, is on the authority of Rose. (Poggen. Annalen ix. 367.)

Phosphorous Acid.—When phosphorus is burned in air highly rarefied, imperfect oxidation ensues, and metaphosphoric and phosphorous acids are generated, the latter being obtained in the form of a white volatile powder. In this state it is anhydrous. Heated in the open air, it takes fire, and forms metaphosphoric acid; but if exposed to heat in close vessels, it is resolved into metaphosphoric acid and phosphorus. It dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalies, and forms salts which are termed *phosphites*. The solution of phosphorous acid absorbs oxygen slowly from the air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold from their saline combinations in the metallic form. Nitric acid converts it into phosphoric acid.

Phosphorous acid may be procured more conveniently by subliming phosphorus through powdered bichloride of mercury contained in a glass tube; when a limpid liquid comes over, which is a compound of chlorine and phosphorus. (Davy's Elements, p. 288.) This substance and water mutually decompose each other: the hydrogen of water unites with the chlorine, and forms hydrochloric acid; while the oxygen attaches itself to the phosphorus, and thus phosphorous acid is produced. The solution is then evaporated to the consistence of syrup to expel the hydrochloric acid; and the residue, which is hydrate of phosphorous acid, becomes a crystalline solid on cooling. When this hydrate is heated in close vessels, the elements of the water and acid react on each other, forming metaphosphoric acid and a gaseous compound of hydrogen and phosphorus. The nature of this gas will be more particularly noticed in the section on phosphuretted hydrogen.

Phosphorous acid is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oil-like liquid. Dulong thinks that a distinct acid is generated in this case, which he calls *phosphatic acid;* but the opinion of Davy, that it is merely a mixture of phosphoric and phosphorous acids, is in my opinion perfectly correct.

Phosphoric Acid.—It was shown in the year 1827 by Dr. Clarke, now Professor of chemistry in Aberdeen, that under the term *phosphoric acid* had previously been confounded two distinct acids, one of which he proposed to distinguish by the name of *pyrophosphoric acid* (from *πυρ fire*), to indicate that it is phosphoric acid modified by heat; and very lately Mr. Graham has described another modification of phosphoric acid, to which he has given the provisional name of metaphosphoric (from *μετα together with*), implying phosphoric acid and something besides; but this name is rather unfortunate, since it is applied to the only one of the three modifications which can be obtained free from water. Perhaps paraphosphoric (from *παρα near to*) would be more appropriate. These three acids contain phosphorus and oxygen in the same ratio, and have the same equivalent, so that they may be considered as isomeric bodies (page 152); but that difference in the arrangement of their elements on which their peculiarities may be presumed to depend, is very slight, since they are easily convertible into each other. Mr. Graham, indeed, supposes the difference to arise solely from a disposition to unite in different proportions with water and alkaline bases; but this view scarcely suffices as an explanation, because it does not account for the peculiar *disposition* which causes their distinctive characters. (Phil. Trans. 1833, Part ii., and Phil. Mag. 3rd Series, iv. 401.)

Phosphoric acid has hitherto been obtained only in combination with water or some alkaline base. One of the best modes for procuring it, is to oxidize phosphorus by strong nitric acid; but in this process care is necessary, as the action is sometimes very violent, and the escape of binoxide of nitrogen gas ungovernably rapid. It is safely conducted by adding fragments of phosphorus, or the so-called phosphatic acid, to strong nitric acid contained in a platinum crucible partially closed by its cover. Gentle heat is applied so as to commence, and, when necessary, to maintain moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness, and exposed to a red heat to expel the last traces of nitric acid. This should always be done in vessels of platinum, since phosphoric acid acts chemically upon those of glass or porcelain, and is thereby rendered impure. In this case, as in some other instances of the oxidation of combustibles by nitric acid, water is decomposed; and while its oxygen unites with phosphorus, its hydrogen combines with nitrogen of the nitric acid. A portion of ammonia, thus generated, is expelled by heat in the last part of the process.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this purpose, superphosphate of lime, obtained in the way already described, should be boiled for a few minutes with excess of carbonate of ammonia. The lime is thus precipitated as a phosphate, and the solution contains phosphate, together with a little sulphate of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which means the ammonia and sulphuric acid are expelled.

In both the foregoing processes phosphoric acid exists only in solution; for on heating to redness in order to expel ammonia in the one case and nitric acid in the other, metaphosphoric acid is generated. To reproduce the phosphoric acid the residue in the crucible requires to be dissolved in water and boiled for a few minutes.

Phosphoric acid is colourless, intensely sour to the taste, reddens litmus strongly, and neutralizes alkalies; but it does not destroy the texture of the skin like sulphuric and nitric acids. Its solution may be evaporated at a temperature of 300° without decomposition, and when thus concentrated it assumes a dark colour, is as thick as treacle when cold, and consists of 71.4 parts or one eq. of phosphoric acid, and 27 parts or three equivalents of water. Mr. Graham obtained this hydrate in thin crystalline plates, which were extremely deliquescent, by keeping it for seven days in *vacuo* along with sulphuric acid. On heating this hydrate for several days to 415°, it lost nearly two-thirds of an equivalent of water, and then principally consisted of pyrophosphoric acid with two equivalents of water. At a still higher temperature metaphosphoric acid began to be formed; and at a red heat the conversion was complete. But after ignition it still contains water, amounting according to Rose to 9.44 per cent, which is rather more than an equivalent of water to one of metaphosphoric acid.

Phosphoric acid is remarkable for its tendency to unite with alkaline bases, in such proportions that the oxygen of the base and of the acid is as 3 to 5; or, in other words, it is prone to form subsalts, in which one equivalent of acid is combined with three equivalents of base. It manifests the same character in regard to water, and ceases to be phosphoric acid unless three equivalents of water to one of acid are present: it even appears that the water acts the part of a base, hence called *basic* water, and that the aqueous solution is not a mere solution of phosphoric acid, but of triphosphate of water, a sort of salt composed of one equivalent of acid and three equivalents of water. Part of this basic water enters along with soda into the constitution of two of the phosphates of soda, the water and soda together forming the three equivalents of base required by one equivalent of the acid. This point will be more fully described in the history of the phosphates.

When phosphoric acid is neutralized by ammonia and mixed with nitrate of oxide of silver, the yellow phosphate of that oxide subsides, a character by which it is distinguished from pyrophosphoric and metaphosphoric acids, as well as from all other acids except the arsenious. A certain test between phosphoric and arsenious acids is, that the former is neither changed in colour nor precipitated when a stream of hydrosulphuric acid gas is transmitted through it; while the latter, with the required precautions, first acquires a yellow tint, and then yields a yellow precipitate.

Pyrophosphoric Acid.—This acid is formed by exposing concentrated phosphoric acid for some time to a heat of 415°. Its general characters resemble phosphoric acid; but when neutralized by ammonia and mixed with nitrate of oxide of silver, it yields a snow-white granular precipitate, pyrophosphate of that oxide, by which it is distinguished from phosphoric and metaphosphoric acids. In solution with cold water pyrophosphoric acid passes gradually, and at a boiling temperature rapidly, into phosphoric acid. Its salts, while neutral, are very permanent; but when boiled with either of the stronger acids in water, they are quickly converted more or less completely into phosphates.

Pyrophosphoric acid is remarkable for its tendency to unite with two equivalents of a base. Its aqueous solution probably contains a dipyrophosphate of water, that is one equivalent of the acid with two eq. of water, expressed by $2\dot{H} + \underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$ or $\dot{H}^2\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$. This basic water is readily displaced by two equivalents of stronger bases, such as soda; or if one equivalent only of soda be added, then the soda and water together make up the two equivalents of base, the formula of the salt being $\dot{Na}\dot{H}\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$. The readiest mode of obtaining a pyrophosphate is to heat phosphoric acid with any fixed base in the ratio of one to two of their equivalents. This was done by Dr. Clarke in the experiments by which he established the existence of pyrophosphoric acid. (Brewster's Journal, vii. 298.) Phosphate of soda is a compound of one eq. phosphoric acid, two eq. soda, one eq. basic water, and twenty-four eq. water of crystallization, its formula being $\dot{\mathrm{Na}}^2\dot{\mathrm{H}}\,\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}} + \dot{\mathrm{H}}^{24}$: on drying this salt its water of crystallization is expelled and there remains $\dot{\mathrm{Na}}^2\dot{\mathrm{H}}\,\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}}$, which is still a phosphate; but on heating to redness the basic water is expelled, and $\dot{\mathrm{Na}}^2\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}}$, pyrophosphate of soda, remains. By being forced to unite with two equivalents of base, the acid acquires a disposition to do so on all occasions.

Metaphosphoric Acid.—This acid is obtained by burning phosphorus in dry air or oxygen gas, or heating to redness a concentrated solution of phosphoric or pyrophosphoric acids. By the former method, the acid is a white solid, and anhydrous; in the latter it is a hydrate, or probably a metaphosphate of water, composed of one eq. acid and one eq. water, its formula being $\dot{\mathrm{H}}\,\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}}$. The water in this compound cannot be expelled by fire, since on attempting to do so by a violent heat, the whole is sublimed. In an open crucible, it volatilizes at a temperature by no means high.

The peculiarity of this acid is to combine with one equivalent of a base. On exposing the anhydrous acid to the air it rapidly deliquesces, and at the same time acquires its basic water, which can only be replaced by an equivalent quantity of soda or some other alkaline base. The water is also driven off by fusion with siliceous or aluminous substances, with which the acid unites and forms very fusible compounds. The pure hydrated acid is of itself very fusible, and on cooling concretes into a transparent brittle solid, being known under the name of *glacial phosphoric acid*, which is highly deliquescent, and can hence only be preserved in its glassy state in bottles carefully closed.

The metaphosphoric resembles pyrophosphoric acid in the facility with which its aqueous solution passes into phosphoric acid. On the contrary, both of the other acids are converted into metaphosphates when heated to redness in contact with no more than one equivalent of certain fixed bases, such as potassa and soda. This acid when free occasions precipitates in solutions of the salts of baryta, and most of the earths and metallic oxides, and forms an insoluble compound with albumen. The metaphosphate of baryta and oxide of silver both fall in gelatinous flakes of a gray colour.

SECTION IX.

BORON.

SIR H. DAVY discovered the existence of *boron* in 1807 by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of it for determining its properties. Gay-Lussac and Thenard* procured it in greater quantity in 1808, by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free. The easiest and most economical method of preparing this substance, according to Berzelius, is to decompose borofluoride of potassium or sodium by means of potassium. (Annals of Philosophy, xxvi. 128.)

Boron is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water whether hot or cold. It bears intense heat in close vessels, without fusing or undergoing any other change except a slight increase of density. Its specific gravity is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600°, it suddenly takes fire oxygen gas disappears, and boracic acid is generated. It is very difficult to oxidize all the boron by burning, because the boracic acid fuses at the moment of being formed, and by glazing the surface of the unburned boron protects it from oxidation. It also passes into boracic acid when heated with nitric acid, or with any substance that yields oxygen with facility.

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* Recherches Physico-Chimiques, vol. i.

According to the experiments of Davy and Berzelius, boron in burning unites with 200 per cent. of oxygen; and the latter, from the composition of borax, estimates the oxygen in boracic acid at 68.8 per cent. Adopting this estimate, and regarding boracic acid as a compound of one equivalent of boron to three eq. of oxygen, the equivalent of boron is inferred from the proportion, as 68.8 : 31.2 : : 24 : 10.9. In this, as in some other cases, where a combustible unites with oxygen in one proportion only, it is difficult with any certainty to assign the true atomic constitution of the compound. Boracic acid may be a compound of boron and oxygen in the ratio of one atom to one atom, in that of one to two as supposed by Dr. Thomson, or of one to three. The latter appears to me most consistent with other compounds of boron. Hence boracic acid is thus constituted:—

	Boron.		Oxygen.	Equiv.	Formula.
Boracic acid	10.9 or 1 eq.	+	24 or 3 eq.	= 34.9	$B + 3O$ or $\dddot{B}$.

Boracic Acid.—This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, a native compound of boracic acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a solution of purified borax in about four times its weight of boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boracic acid is deposited, when the solution cools, in a confused group of shining scaly crystals. It is then thrown on a filter, washed with cold water to separate the adhering sulphate of soda and sulphuric acid, and still further purified by solution in boiling water and re-crystallization. But even after this treatment it is apt to retain a little sulphuric acid; and on this account, when required to be absolutely pure, it should be fused in a platinum crucible, and once more dissolved in hot water and crystallized.

Boracic acid in this state is a hydrate, which contains 43.62 per cent. of water, being a ratio of 34.9 parts or one equivalent of the anhydrous acid to 27 parts or three eq. of water. This hydrate dissolves in 25.7 times its weight of water at 60°, and in 3 times at 212°. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boracic acid. Its specific gravity is 1.479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. Mr. Faraday has noticed that it renders turmeric paper brown like the alkalies. From the weakness of its acid properties, all the borates, when in solution, are decomposed by the stronger acids.

When hydrous boracic acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains which bears a white heat without being sublimed. On cooling, it forms a hard, colourless, transparent glass, which is anhydrous boracic acid. If the water of crystallization be driven off by the sudden application of a strong heat, a large quantity of boracic acid is carried away during the rapid escape of watery vapour. The same happens, though in a less degree, when a solution of boracic acid in water is boiled briskly.

Vitrified boracic acid should be preserved in well-stopped vessels; for if exposed to the air, it absorbs water, and gradually loses its transparency. Its specific gravity is 1.803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

SECTION X.

SELENIUM.

This substance was discovered in 1818 by Berzelius, who called it selenium, from Σελήνη, *the Moon*, suggested by its having at first been mistaken for the metal tellurium. (An. de Ch. et de Ph. ix. 160, and An. of Phil. xiii. 401.) It has hitherto been obtained in very small quantity, and occurs for the most part in combination with some varieties of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal in the Hartz, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. Berzelius found it in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid, at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium. For the extraction of selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid; while the selenium either sublimes as such or in the state of selenious acid. Should any of the latter be carried over into the water, it would there be reduced by the sulphurous acid.

Selenium, at common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead when in mass: but it is of a deep red colour when reduced to powder. Its specific gravity is between 4.3 and 4.32. At 212° it softens, and is then so tenacious that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but is free from odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar-red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but, since it is an imperfect conductor of heat and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, oxide of selenium and selenious acid, are generated. If exposed to the oxidizing part of the blow-pipe flame, it tinges the flame with a light blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

Berzelius has shown that selenic acid is composed of 24 parts of oxygen and 39.6 of selenium. This substance, also, has three grades of oxidation, the oxygen in the two last of which is in the ratio of 2 and 3; and the highest grade, selenic acid, has in all its chemical relations a singularly close analogy to sulphuric acid. From these facts it is inferred that selenic acid is composed of one atom of selenium and three atoms of oxygen, and that the equivalent of the former is 39.6.

The compounds of selenium described in this section are the following:—

	Selenium.	Oxygen.	Equiv.	Formulæ.
Oxide of selenium (probably)	39.6 or 1 eq. +	8 or 1 eq. =	47.6	$Se+O$ or $\dot{Se}$.
Selenious acid . .	39.6	+16 or 2 eq. =	55.6	$Se+2O$ or $\ddot{Se}$.
Selenic acid . .	39.6	+24 or 3 eq. =	63.6	$Se+3O$ or $\dddot{Se}$.

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and by washing the product to separate selenious acid, which is generated at the same time. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-hydrochloric acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites.*

Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous is converted into sulphuric acid. Hydrosulphuric acid also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

Selenic Acid.—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has been described in elementary works under the name of selenic acid; but the recent discovery of another acid of selenium containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of selenic acid was first noticed by M. Nitzsch, assistant of Mitscherlich, and its properties have been examined and described by the Professor himself. (Edin. Journal of Science, viii. 294.)

This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. Seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with hydrochloric acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only seleniate of soda, together with nitrate and nitrite of soda; while the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while, on cooling, nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact, that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° than at higher or lower temperatures. The nitrite of soda, formed during the fusion, is purposely reconverted into nitrate by digestion with nitric acid.

The seleniate of soda thus procured always contains a little sulphuric acid, derived from the metallic sulphurets of the ore; and it is not possible to separate this acid by crystallization. All attempts to separate it by means of baryta were likewise fruitless; and the only method of effecting this object is by reducing the selenic acid into selenium. This is done by heating a mixture of seleniate of soda with hydrochlorate of ammonia, when the sodium unites with chlorine, all the hydrogen with oxygen, and selenium and nitrogen are set free. This change will be more readily followed when stated in symbols;—thus

$$Na+O, Se+3O, N+3H, \text{ and } H+Cl, \text{ yield } N, Se, 4(H+O), \text{ and } Na+Cl.$$

The selenium which sublimes is quite free from sulphur. It is then converted by nitric acid into selenious acid, which should be neutralized with soda, and fused with nitre or nitrate of soda. The pure seleniate of soda, separated from the nitrate according to the foregoing process, is subsequently dissolved in water, and obtained in crystals by spontaneous evaporation.

To procure the acid in a free state, seleniate of soda is decomposed by nitrate of oxide of lead. The seleniate of that oxide, which is as insoluble as the sulphate, after being well washed, is exposed to a current of hydrosulphuric acid gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of the gas is driven off by heat, and pure selenic acid remains diluted with water. The absence of fixed substances may be proved by its being volatilized by heat without residue; and if free from sulphuric acid, it gives no precipitate with chloride of barium after being boiled with hydrochloric acid.* Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Selenic acid is a colourless liquid, which may be heated to 536° without appreciable decomposition; but above that point decomposition commences, and it becomes rapid at 554°, giving rise to disengagement of oxygen and selenious acid. When concentrated by a temperature of 329° its specific gravity is 2.524; at 512° it is 2.60, and at 545° it is 2.625, but a little selenious acid is then present. When procured by the process above described, selenic acid always contains water, but it is very difficult to ascertain its precise proportion. Some acid, which had been heated higher than 536°, contained, subtracting the quantity of selenious acid present, 15.75 per cent. of water, which approximates to the ratio of one equivalent of water and one of the acid. It is certain that selenic acid is decomposed by heat before parting with all the water which it contains.

Selenic acid has a powerful affinity for water, and emits as much heat in uniting with it as sulphuric acid does. Like this acid it is not decomposed by hydrosulphuric acid, and hence this gas may be employed for decomposing seleniate of the oxides of lead or copper. With hydrochloric acid the change is peculiar; for on boiling the mixture, mutual decomposition ensues, water and selenious acid are formed, and chlorine is set free; so that the solution, like *aqua regia*, is capable of dissolving gold and platinum. Selenic acid dissolves zinc and iron with disengagement of hydrogen gas, and copper with formation of selenious acid. It dissolves gold also, but not platinum. Sulphurous acid has no action on selenic acid, whereas selenious acid is easily reduced by it. Consequently, when it is wished to precipitate selenium from selenic acid, it must be boiled with hydrochloric acid before sulphurous acid is added.

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* The necessity for this previous boiling with hydrochloric acid is to convert the selenic into selenious acid, without which change the chloride of barium would produce a precipitate of seleniate of baryta. The rationale of the action of hydrochloric acid is explained further on. *Ed.*

Mitscherlich has observed, that selenic and sulphuric acids are not only analogous in composition and in many of their properties, but that the similarity runs through their compounds with alkaline substances, their salts resembling each other in chemical properties, constitution, and form.

SECTION XI.

CHLORINE.

The discovery of chlorine was made in the year 1774 by Scheele, while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid.* The French chemists called it *oxygenized muriatic acid*, a term which was afterwards contracted to *oxy-muriatic acid*, from an opinion proposed by Berthollet that it is a compound of *muriatic acid* and oxygen. In 1809 Gay-Lussac and Thenard published an abstract of some experiments upon this substance, which subsequently appeared at length in their Recherches Physico-Chimiques, wherein they stated that oxymuriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Sir H. Davy engaged in the inquiry about the same time; and after having exposed oxy-muriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society an essay, in which he denied its compound nature; and he maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now universally received by chemists. The grounds of preference will hereafter be briefly stated.

Chlorine gas is obtained by the action of hydrochloric acid on peroxide of manganese. The most convenient method of preparing it is by mixing concentrated hydrochloric acid, contained in a glass flask, with half its weight of finely powdered peroxide of manganese. Effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected in inverted glass bottles filled with warm water; and when the water is wholly displaced by the gas, the bottles should be closed with a well-ground glass stopper. As some hydrochloric acid gas commonly passes over with it, the chlorine should not be considered quite pure, till after being transmitted through water.

The theory of this process will be readily understood by first viewing the elements which act on each other, namely,—

Manganese .	27.7 or 1 eq.	Mn	Chlorine .	70.84	or 2 eq.	$2Cl$
Oxygen .	16 2 eq.	$2O$	Hydrogen	2	or 2 eq.	$2H$
Perox. of mang.	43.7 or 1 eq.	$Mn+2O$.	Hydroch. ac.	72.84	or 2 eq.	$2(H+Cl)$;

and then inspecting the products derived from them, namely,

Manganese . .	27.7 .	Hydrogen	2	Chlorine 35.42 or 1 eq.
Chlorine . .	35.42 .	Oxygen	16	
Chloride of mang.	63.12	Water	18.	

In symbols

$$Mn+2O, \text{ and } 2(H+Cl) \text{ yield } Mn+Cl,\ 2(H+O), \text{ and } Cl.$$

The affinities which determine these changes are the mutual attraction of oxygen and hydrogen, and of chlorine and manganese.

When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner. Three parts of sea-salt are intimately mixed with one of peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are added. By the action of sulphuric acid on sea-salt, hydrochloric acid is disengaged, which reacts as in the former case upon the peroxide of manganese; so that, instead of adding hydrochloric acid directly to the manganese, the materials for forming it are employed. In this process, however, the sulphates of soda and protoxide of manganese are generated, instead of chloride of manganese. Thus the materials which act on each other are $\ddot{Mn}$, $Na + Cl$, and $2\dddot{S}$; and the products $\dot{Mn} + \dddot{S}$, $\dot{Na} + \dddot{S}$; and Cl.

Chlorine (from χλωρος, green) is a yellowish-green coloured gas, which has an astringent taste and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, the latter being solely due, as in the case of air and oxygen, to the chlorine acting chemically on the oil with which the compressing apparatus is lubricated. (An. de Ch. et de Ph. xliv. 181.) According to Davy 100 cubic inches of dry chlorine, at 30 Bar. and 60° F. weigh between 76 and 77 grains. Gay-Lussac and Thenard found the density of pure and dry chlorine to be 2.47, which gives 76.5988 grains as the weight of 100 cubic inches at 60° F. and 30 Bar. Under the pressure of about four atmospheres, it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed. Mr. Kemp finds that this liquid is a non-conductor of electricity.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by transmitting a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of 32°, yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Mr. Faraday, of 35.42 parts or one equivalent of chlorine, and 90 parts or ten equivalents of water.

Chlorine experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but if water be present, the chlorine decomposes that liquid, unites with the hydrogen to form hydrochloric acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused daylight, and not at all when light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a supporter of combustion. If a lighted taper be plunged into chlorine gas, it burns for a short time with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously, and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena, to which chlorine gives rise, are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red heat; and most compound substances, of which hydrogen is an element, are deprived of that principle, and, therefore, decomposed in like manner. For the same reason, when chlorine, water, and some other body which has a strong affinity for oxygen, are presented to one another, water is usually resolved into its elements, its hydrogen attaching itself to the chlorine, and its oxygen to the other body. Hence it happens that chlorine is, indirectly, one of the most powerful oxidizing agents which we possess.

When any compound of chlorine and an inflammable is exposed to the influence of galvanism, the inflammable body goes over to the negative, and chlorine to the positive pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Chlorine, though formerly called an acid, possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows comparatively little disposition to unite with alkalies. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal.

The mutual action of chlorine and the pure alkalies leads to complicated changes. If chlorine gas be passed into a solution of potassa till all alkaline reaction cease, a liquid is obtained which has the odour of a solution of chlorine in water. But on applying heat, the chlorine disappears entirely, and the solution is found to contain chlorate of potassa and chloride of potassium. From six equivalents of chlorine and six eq. of potassa are obtained five eq. of chloride of potassium and one eq. of chlorate of potassa, the oxygen of five eq. of potassa just sufficing to form chloric acid with one eq. of chlorine; or, stating the same in symbols,

$$6Cl \text{ and } 6(K+O) \text{ yield } 5(K+Cl),\ K+O, \text{ and } Cl+5O.$$

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Davy proved that chlorine cannot bleach unless water is present. Thus dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also that hydrochloric acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen and of chromic and permanganic acids, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in destroying the volatile principles given off by putrefying animal matter; and it probably acts in a similar way on contagious effluvia. A peculiar compound of chlorine and soda, the nature of which will be considered in the section on sodium, has been lately introduced for this purpose by M. Labarraque.

Chlorine is in general easily recognized by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of nitrate of oxide of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia. The whole of the chlorine, however, is not thrown down; for the oxygen of the oxide of silver unites with a portion of chlorine, and converts it into chloric acid.

Those compounds of chlorine, which are not acid, are termed *chlorides* or *chlorurets*. The former expression, from the analogy between chlorine and oxygen, is perhaps the more appropriate.

Berzelius inferred the equivalent of chlorine from the oxygen lost by chlorate of potassa when decomposed by heat, and the quantity of chlorine found in the residual chloride of potassium. I investigated the same subject by examining into the composition of the nitrate of the oxide and chloride of silver, of the protoxide and chloride of lead, and of the peroxide and chlorides of mercury. These researches concur in showing 35.42 to be the equivalent of chlorine, and not 36, the number commonly adopted in this country. The number inferred from the densities of chlorine and hydrogen gases is 35.84 (page 146); but, unfortunately, the densities of these gases are not known with the precision required for an application of this nature.

The composition of the compounds described in this section is as follows:

	Chlorine.				Equiv.	Formulæ.
Hydrochloric acid	35.42	1 eq. + Hydrogen	1	1 eq. =	36.42	$H+Cl$
Protoxide of chlorine	35.42	+ Oxygen	8	1 eq. =	43.42	$Cl+O$
Peroxide of chlorine	35.42	+ Ditto	32	4 eq. =	67.42	$Cl+4O$
Chloric acid	35.42	+ Ditto	40	5 eq. =	75.42	$Cl+5O$
Perchloric acid*	35.42	+ Ditto	56	7 eq. =	91.42	$Cl+7O$
Quadrochloride of nitrogen	141.68	4 eq. + Nitrogen	14.15	1 eq. =	155.83	$N+4Cl$
Protochloride of carbon	35.42	1 eq. + Carbon	6.12	1 eq. =	41.54	$C+Cl$
$\frac{5}{4}$ Chloride of carbon	177.1	5 eq. + Ditto	24.48	4 eq. =	201.58	$4C+5Cl$
Dichloride of carbon	35.42	1 eq. + Ditto	12.24	2 eq. =	47.66	$2C+Cl$
Perchloride of carbon	106.26	3 eq. + Ditto	12.24	2 eq. =	118.5	$2C+3Cl$
Dichloride of sulphur	35.42	1 eq. + Sulphur	32.2	2 eq. =	67.62	$2S+Cl$
Protochloride of sulphur	35.42	1 eq. + Ditto	16.1	1 eq. =	51.52	$S+Cl$
Sesquichloride of phosphorus	106.26	3 eq. + Phosph.	31.4	2 eq. =	137.66	$2P+3Cl$
Perchloride of phosphorus	177.1	5 eq. + Ditto	31.4	2 eq. =	208.5	$2P+5Cl$
Chlorocarbonic acid gas	35.42	1 eq. + Carb. ox.	14.12	1 eq. =	49.54	$\dot{C}+Cl$
Chloral	212.52	6 eq. + Carbon Oxygen	55.08 32	9 eq. 4 eq.	= 299·6	$9Cl+6Cl$ $+4O$
Terchloride of boron	106.26	3 eq. + Boron	10.9	1 eq. =	117.16	$B+3Cl$

Hydrochloric Acid.—A concentrated aqueous solution of this acid has been long known under the names of spirit of salt, and of marine or muriatic acid; but in its purer form of gas, it was discovered in 1772 by Dr. Priestley. It may be conveniently prepared by putting an ounce of strong hydrochloric acid solution into a glass flask, and heating it by means of a lamp till the liquid boils, when the gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of concentrated sulphuric acid on an equal weight of sea-salt. Brisk effervescence ensues at the moment of making the mixture, and on the application of heat, a large quantity of hydrochloric acid gas is disengaged. In the former process, hydrochloric acid, previously dissolved in water, is simply expelled from the solution by heat. The explanation of the latter process is more complicated. Sea-salt was formerly supposed to be a compound of hydrochloric acid and soda; and, on this supposition, the soda was believed merely to quit the hydrochloric and unite with sulphuric acid. But the researches of Gay-Lussac, Thenard, and Davy proved that it consists of chlorine and sodium combined in the ratio of their equivalents. The nature of its action with sulphuric acid will be understood by comparing the elements concerned in the change before and after it has occurred:—

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* *Oxychloric* would be a more appropriate appellation for this acid, as its adoption would prevent all ambiguity in naming its salts. This name I proposed for it in 1819, in my System of Chemistry for Students of Medicine; and it may be inferred that it has the sanction of Berzelius, as he employs it in his *Traité de Chimie.—Ed.*

Hydrous Sulp. Acid.			Chloride of Sodium.		Sulp. of Soda.			Hydrochloric Acid.	
Real acid		40.1	Chlorine	35.42	Acid		40.1	Chlorine	35.42
Water	Hyd.	1	Sodium	23.3	Soda	Sod.	23.3	Hydrogen	1
	Oxy.	8				Oxy.	8		

Or in symbols,

$(S+3O)+(H+O)$, and $Na+Cl$, yield $(Na+O)+(S+3O)$, and $H+Cl$.

Thus it appears that single equivalents of water, sulphuric acid, and chloride of sodium, yield sulphate of soda and hydrochloric acid. The water of the sulphuric acid is essential; so much so, indeed, that chloride of sodium is not decomposed at all by anhydrous sulphuric acid.

Hydrochloric acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and hydrochloric acid is generated. A similar effect is produced by flame, by a red-hot body, and by spongy *platinum*. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place; but if exposed to the diffused light of day, gradual combination ensues, which is completed in the course of 24 hours. The direct solar rays produce, like flame and electricity, sudden inflammation of the whole mixture, accompanied with explosion; and, according to Mr. Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

The experiments of Davy, and Gay-Lussac and Thenard concur in proving that hydrogen and chlorine gases unite in equal volumes, and that the hydrochloric acid, which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of hydrochloric acid is easily inferred. For, as

		Grains.
50 cubic inches of chlorine weigh	.	38.2994
50 hydrogen	. .	1.0683
100 cubic inches of muriatic acid gas must weigh		39.3677

These numbers are nearly in the ratio of 1 to 35.42, being that of single equivalents of chlorine and hydrogen, as stated at page 146. The specific gravity of hydrochloric acid gas calculated from the same facts (page 148) is 1.2694, which agrees closely with direct observations.

Hydrochloric acid gas is colourless, and has a pungent odour and an acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50°, it is liquid. It is quite irrespirable, exciting violent spasm of the glottis; but when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, nor is the gas itself inflammable.

Hydrochloric acid gas is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the negative, and chlorine at the positive pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not affected by oxygen under common circumstances; but if a mixture of oxygen and hydrochloric acid gases is electrified, the oxygen unites with the hydrogen of the acid to form water, and chlorine is set at liberty. For this and the preceding fact, we are indebted to the researches of Dr. Henry.

One of the most striking properties of hydrochloric acid gas is its powerful attraction for water. A dense white cloud appears whenever it escapes into the air, owing to its combining with the aqueous vapour of the atmosphere. When a piece of ice is put into a jar full of the gas confined over mercury, the ice liquefies on the instant, and the whole of the gas disappears in the course of a few seconds. On opening a long wide jar of hydrochloric acid gas under water, the absorption of the gas takes place so instantaneously, that the water is forced up into the jar with the same violence as into a vacuum.

Hydrochloric acid is much used in the form of a concentrated aqueous solution, which is made by transmitting a current of the gas into water as long as any of it is absorbed. Considerable increase of temperature takes place during the absorption, and, therefore, the apparatus should be kept cool by ice. Davy states (Elements, p. 252.) that water at the temperature of 40° absorbs 480 times its volume of the gas, and that the solution has a density of 1.2109. Dr. Thomson finds that one cubic inch of water at 69° absorbs 418 cubic inches of gas, and occupies the space of 1.34 cubic inch. The solution has a density of 1.1958, and one cubic inch of it contains 311.04 cubic inches of hydrochloric acid gas. The quantity of real acid contained in solutions of different densities may be determined by ascertaining the quantity of pure marble dissolved by a given weight of each. Every 50.62 grains of marble correspond to 36.42 of real acid. The following table from Dr. Thomson's "Principles of Chemistry," is constructed according to this rule. The first and second columns show the atomic constitution of each acid.

Table exhibiting the Specific Gravity of Muriatic Acid of determinate Strengths.

Atoms of acid.	Atoms of water.	Real acid in 100 of the liquid.	Specific Gravity.	Atoms of acid.	Atoms of water.	Real acid in 100 of the liquid.	Specific Gravity.
1	6	40.659	1.203	1	14	22.700	1.1060
1	7	37.000	1.179	1	15	21.512	1.1008
1	8	33.945	1.162	1	16	20.442	1.0960
1	9	31.346	1.149	1	17	19.474	1.0902
1	10	29.134	1.139	1	18	18.590	1.0860
1	11	27.206	1.1285	1	19	17.790	1.0820
1	12	25.517	1.1197	1	20	17.051	1.0780
1	13	24.026	1.1127				

All the Pharmacopœias give directions for forming hydrochloric acid. The process recommended by the Edinburgh College is practically good. The proportions they recommend are equal weights of sea-salt water, and sulphuric acid, more acid being purposely employed than is sufficient to form a neutral sulphate with the soda, so that the more perfect decomposition of the sea-salt may be ensured. The acid, to prevent too violent effervescence at first, is mixed with one-third of the water, and when the mixture has cooled, it is poured upon the salt previously introduced into a glass retort. The distillation is continued to dryness; and the gas, as it escapes, is conducted into the remainder of the water. The theory of the process has already been explained. The residue is a mixture of sulphate and bisulphate of soda. The specific gravity of the acid obtained by this process is 1.170.

Hydrochloric acid of commerce has a yellow colour, and is always impure. Its usual impurities are nitric acid, sulphuric acid, and oxide of iron. The presence of nitric acid may be inferred if the hydrochloric acid has the property of dissolving gold-leaf. Iron may be detected by ferrocyanuret of potassium, and sulphuric acid by chloride of barium, the suspected hydrochloric acid being previously diluted with three or four parts of water. The presence of nitric acid is provided against by igniting the sea-salt, as recommended by the Edinburgh College, in order to decompose any nitre which it may contain. The other impurities may be avoided by employing Woulfe's Apparatus. A few drachms of water are put into the first bottle to retain the chloride of iron and sulphuric acid which pass over, and the hydrochloric acid gas is condensed in the second.

A strong solution of pure hydrochloric acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and neutralizes alkalies. It combines with water in every proportion, and causes increase of temperature when mixed with it, though in a much less degree than sulphuric acid. It freezes at —60° F.; and boils at 110°, or a little higher, giving off pure hydrochloric acid gas in large quantities.

Hydrochloric acid is decomposed by substances which yield oxygen readily. Thus several peroxides, such as those of manganese, cobalt, and lead, effect its decomposition. Chloric, iodic, bromic, nitric, and selenic acids act on the same principle. A mixture of nitric and hydrochloric acids, in the ratio of one measure of the former to two of the latter, has long been known under the name of *aqua regia*, as a solvent for gold and platinum. When these acids are mixed together, the solution instantly becomes yellow; and on heating the mixture, pure chlorine is evolved, and the colour of the solution deepens. On continuing the heat, chlorine and nitrous acid vapours are disengaged. At length the evolution of chlorine ceases, and the residual liquid is found to be a solution of hydrochloric and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, that nitric and hydrochloric acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine; while hydrochloric and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitro-hydrochloric acid in dissolving gold is owing to the chlorine which is liberated. (Davy in the Quarterly Journal, vol. i.)

Hydrochloric acid is distinguished by its odour, volatility, and strong acid properties. With nitrate of oxide of silver it yields the same precipitate as chlorine; but no chloric acid is generated, because the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, and the chlorine in consequence is entirely precipitated. Notwithstanding that nitrate of oxide of silver yields the same precipitate with chlorine and hydrochloric acid, there is no difficulty in distinguishing between them; for the bleaching property of the former is a sure ground of distinction.

COMPOUNDS OF CHLORINE AND OXYGEN.

The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for each other. These principles, consequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their separation. Chemists are not agreed as to the exact number of the compounds of chlorine and oxygen. The subjoined list contains those which hitherto have been generally admitted; but the existence of the first is very problematical, while some enumerate a fifth under the name of *chlorous acid*.

Vitrified boracic acid should be preserved in well-stopped vessels; for if exposed to the air, it absorbs water, and gradually loses its transparency. Its specific gravity is 1.803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

SECTION X.

SELENIUM.

This substance was discovered in 1818 by Berzelius, who called it selenium, from Σελήνη, *the Moon*, suggested by its having at first been mistaken for the metal tellurium. (An. de Ch. et de Ph. ix. 160, and An. of Phil. xiii. 401.) It has hitherto been obtained in very small quantity, and occurs for the most part in combination with some varieties of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal in the Hartz, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. Berzelius found it in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid, at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium. For the extraction of selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid; while the selenium either sublimes as such or in the state of selenious acid. Should any of the latter be carried over into the water, it would there be reduced by the sulphurous acid.

Selenium, at common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead when in mass: but it is of a deep red colour when reduced to powder. Its specific gravity is between 4.3 and 4.32. At 212° it softens, and is then so tenacious that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but is free from odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar-red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but, since it is an imperfect conductor of heat and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, oxide of selenium and selenious acid, are generated. If exposed to the oxidizing part of the blow-pipe flame, it tinges the flame with a light blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

Berzelius has shown that selenic acid is composed of 24 parts of oxygen and 39.6 of selenium. This substance, also, has three grades of oxidation, the oxygen in the two last of which is in the ratio of 2 and 3; and the highest grade, selenic acid, has in all its chemical relations a singularly close analogy to sulphuric acid. From these facts it is inferred that selenic acid is composed of one atom of selenium and three atoms of oxygen, and that the equivalent of the former is 39.6.

The compounds of selenium described in this section are the following:—

	Selenium.	Oxygen.	Equiv.	Formulæ.
Oxide of selenium (probably)	39.6 or 1 eq.	+ 8 or 1 eq.	= 47.6	$Se+O$ or $\dot{Se}$.
Selenious acid . .	39.6	+ 16 or 2 eq.	= 55.6	$Se+2O$ or $\ddot{Se}$.
Selenic acid . .	39.6	+ 24 or 3 eq.	= 63.6	$Se+3O$ or $\dddot{Se}$.

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and by washing the product to separate selenious acid, which is generated at the same time. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-hydrochloric acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites.*

Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous is converted into sulphuric acid. Hydrosulphuric acid also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

Selenic Acid.—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has been described in elementary works under the name of selenic acid; but the recent discovery of another acid of selenium containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of selenic acid was first noticed by M. Nitzsch, assistant of Mitscherlich, and its properties have been examined and described by the Professor himself. (Edin. Journal of Science, viii. 294.)

This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. Seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with hydrochloric acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only seleniate of soda, together with nitrate and nitrite of soda; while the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while, on cooling, nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact, that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° than at higher or lower temperatures. The nitrite o served by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

Chloric acid reddens vegetable blue colours, has a sour taste, and forms neutral salts, called *chlorates*, (formerly *hyperoxymuriates*), with alkaline bases. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine. It gives no precipitate in solution of nitrate of oxide of silver, and hence cannot be mistaken for hydrochloric acid. Its solution may be concentrated by gentle heat, till it acquires an oily consistence, without decomposition: in this state of highest concentration it acquires a yellowish tint, emits an odour of nitric acid, sets fire to paper and other dry organic matter, and converts alcohol into acetic acid. When sharply heated in a retort, part of the acid is resolved into chlorine and oxygen; but another portion, acquiring oxygen from that which is decomposed, is converted into perchloric acid, and then passes over into the receiver in the form of a dense colourless liquid. (Serullas.) Chloric acid is easily decomposed by deoxidizing agents. Sulphurous acid, for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of hydrosulphuric acid, water is generated, while sulphur and chlorine are set free. The power of hydrochloric acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa, which crystallizes in tables and has a pearly lustre, deflagrates like nitre when flung on burning charcoal, and yields peroxide of chlorine by the action of concentrated sulphuric acid. Chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated to redness, and leaves a residue of chloride of potassium. By this mode Gay-Lussac ascertained the composition of chloric acid, as stated in the preceding table. (An. de Chimie, xci.)

Perchloric Acid.—The saline matter which remains in the retort after forming peroxide of chlorine is a mixture of perchlorate and bisulphate of potassa; and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. Perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of perchloric acid.

The existence of perchloric acid was first ascertained by Count Stadion, who found it to be a compound of two volumes or one equivalent of chlorine and seven of oxygen; and this view of its constitution has been confirmed by Gay-Lussac, Serullas, and Mitscherlich. (An. de Ch. et de Ph. viii. ix. xlvi. 297, and xlix. 113.) According to Serullas it is a very stable compound: it may be heated with hydrochloric or sulphuric acid without change, does not set fire to organic substances, and is not decomposed by alcohol. When concentrated it has a density of 1.65, in which state it emits vapour when exposed to the air, absorbs hygrometric moisture powerfully, and boils at 392° F. By admixture with strong sulphuric acid and distilling, Serullas obtained it in the solid form, both massive and in elongated prisms. It hisses when thrown into water, like red-hot iron when quenched.

Of all the salts of perchloric acid, that with potassa is the most insoluble, requiring 65 times its weight of water at 60° for solution. This salt is readily and safely formed by adding chlorate of potassa, well dried and in fine powder, in small portions at a time, to an equal weight of concentrated sulphuric acid, gently warmed in an open vessel. The peroxide of chlorine escapes without danger, and the chlorate is entirely converted into perchlorate and bisulphate of potassa, the latter of which, being very soluble, is easily removed by cold water. Serullas finds that chlorate of potassa, when decomposed by a low heat, is converted into chloride of potassium and perchlorate of potassa; but the temperature must be carefully managed, otherwise the perchlorate itself would be resolved into oxygen and chloride of potassium. The perchlorate thus procured is purified by solution in hot water and crystallization. It is distinguished from chlorate of potassa by not acquiring a yellow tint on the addition of hydrochloric acid. The primary form of its crystals, according to Mitscherlich, is a right rhomboidal prism isomorphous with permanganate of potassa.

Quadrochloride of Nitrogen.—The elements of this compound have a feeble mutual affinity, and do not unite when presented to each other in their gaseous form. The condition which leads to their union is the decomposition of ammonia by chlorine, during which hydrochloric acid is generated by chlorine combining with the hydrogen of ammonia; while the nitrogen of that alkali, in its nascent state, enters into combination with another portion of chlorine. A convenient mode of preparing the quadrochloride of nitrogen is the following. An ounce of hydrochlorate of ammonia is dissolved in 12 or 16 ounces of hot water; and when the solution has cooled to the temperature of 90°, a glass bottle with a wide mouth, full of chlorine, is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour; and in about 20 minutes globules of a yellow fluid are seen *floating* like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of the chloride, as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle.

Quadrochloride of nitrogen, discovered in 1811 by Dulong, (An. de Ch. lxxxvi.) is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Davy. (Phil. Trans. 1813.) Its specific gravity is 1.653. It does not congeal in the intense cold produced by a mixture of snow and salt. It may be distilled at 160°; but at a temperature between 200° and 212° it explodes. It appears from the investigation of Messrs. Porrett, Wilson, and Kirk, that its mere contact with some substances of a combustible nature causes detonation even at common temperatures. This result ensues particularly with oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen. (Nicholson's Journal. xxxiv.)

Sir H. Davy analyzed chloride of nitrogen by means of mercury, which unites with chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one of nitrogen; and it hence follows that, by weight, it consists of four equivalents of chlorine, and one equivalent of nitrogen.*

Perchloride of Carbon.—The discovery of this compound is due to Mr. Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oil-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, hydrochloric acid is set free, and the carbon, at the moment of separation, unites with the chlorine. (Phil. Trans. 1821.)

Perchloride of carbon is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its specific gravity is exactly double that of water. It fuses at 320°, and after fusion it is colourless and very transparent. It boils at 360°, and may be distilled without change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

Perchloride of carbon burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke; but the combustion ceases as soon as it is withdrawn. It burns vividly in oxygen gas. Alkalies do not act upon it; nor is it changed by the stronger acids, such as the hydrochloric, nitric, or sulphuric acids, even with the aid of heat. When its vapour, mixed with hydrogen, is transmitted through a red-hot tube, charcoal is separated, and hydrochloric acid gas evolved. On passing its vapour over the peroxides of metals, such as that of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and metallic chlorides. Most of the metals decompose it also at the temperature of ignition, uniting with its chlorine, and causing deposition of charcoal.

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* Berzelius states the composition of this compound to be three volumes of chlorine to one of nitrogen, corresponding to three equivalents of the former to one of the latter. These proportions, if found to be correct, will render the chloride and iodide of nitrogen analogous in composition.—*Ed.*

The composition of the perchloride of carbon was inferred by Mr. Faraday from the proportions of chlorine and olefiant gas employed in its production, and from the quantity of chloride of copper and carbonic acid generated when its vapour was transmitted over oxide of copper at a red heat.

$\frac{5}{4}$ *Chloride of Carbon.*—This compound, so called to indicate the ratio of its elements, is formed by boiling chloral with a solution of potassa, lime, or baryta; and was discovered by Liebig. The elements which appear to react on each other are, two eq. of chloral or $2(9C+6Cl+4O)$, two eq. of potassa or $2(K+O)$, and five eq. of water or $5\dot{H}$; and the products are two eq. of the chloride of carbon or $2(4C+5Cl)$, two eq. of chloride of potassium or $2(K+Cl)$, and five eq. of formic acid or $5(2\dot{C}+\dot{H})$. The formic acid of course unites with potassa, and the chloride of carbon, being volatile, passes off in vapour. After condensation it is washed repeatedly with pure water, and obtained quite dry by admixture with strong sulphuric acid, and distillation at 212° F. It may also be more conveniently prepared by distilling, from a capacious retort, a mixture of one pound of chloride of lime, three pounds of water, and two or three ounces either of alcohol or pyroacetic spirit.

This chloride is a limpid, colourless liquid, similar in odour and appearance to the oily fluid which chlorine forms with olefiant gas; though in density, volatility, and composition, it is quite different. Its density is 1.48, and it boils at 141° F. It is but feebly combustible, and is not changed at moderate temperatures either by acids or alkalies.

It is freely dissolved by alcohol and ether, and is precipitated from them by water, in which it is quite insoluble. It may be distilled in contact with potassium without change. When its vapour is transmitted over metallic copper, charcoal is deposited, no gas whatever appears, and a metallic chloride is formed. Its composition was inferred from the quantity of chloride of copper and carbonic acid which were produced, when its vapour was transmitted over oxide of copper at a red heat. (An. de Ch. et de Ph. xlix. 146.)

Protochloride of Carbon.—When the vapour of the perchloride is passed through a red-hot glass or porcelain tube, filled with fragments of rock crystal to increase the quantity of heated surface, partial decomposition occurs, chlorine gas escapes, and a vapour which, analyzed by Mr. Faraday by means of oxide of copper, proved to be protochloride of carbon. At common temperatures it is a limpid colourless liquid, which has a density of 1.5526, does not congeal at 0° F., and at 160° or 170° is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat, some of it is resolved into its elements. In its chemical relations it is very analogous to perchloride of carbon.

Dichloride of Carbon.—The only sample of this substance yet obtained was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre and sulphate of iron. It occurs in small, soft, adhesive fibres of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and 450° F. At 250° it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalies; but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke, and fumes of hydrochloric acid gas.

The nature of this substance is shown by the following circumstances. When its vapour is exposed to a red heat, evolution of chlorine gas ensues, and charcoal is deposited. A similar deposition of charcoal is produced by heating it with phosphorus, iron, or tin; and a chloride is formed at the same time. Potassium burns vividly in its vapour with formation of chloride of potassium and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury, a chloride of that metal and carbonic acid are generated. By these means Messrs. Phillips and Faraday ascertained its composition as given at page 212. (An. of Phil. xviii. 150.)

Dichloride of Sulphur.—This compound was discovered in the year 1804 by Dr. Thomson,* and was afterwards examined by Berthollet.† It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated, until nearly all the sulphur disappears. Direct combination ensues, and the product, distilled off from uncombined sulphur, is obtained under the form of a liquid which appears red by reflected, and yellowish-green by transmitted light. Its density is 1.687. It is volatile below 200°, boils at 280°, yielding vapour which has a density of 4.70, and condenses again without change in cooling. When exposed to the air it emits acrid fumes, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalies. It acts with energy on water:—mutual decomposition ensues, with formation of hydrochloric and hyposulphurous acids, and deposite of sulphur, by which the water is rendered cloudy. From a recent analysis by Rose it consists of 35.42 parts or one equivalent of chlorine, and 32.2 parts or two eq. of sulphur. (Pog. Annalen xxi. 431.)

Rose maintains that the preceding is the only chloride of sulphur, arguing that the chloride analyzed by Davy was merely dichloride of sulphur holding chlorine in solution. Dumas, on the other hand, contends, that when sulphur is acted on by excess of chlorine, a chloride of sulphur is really obtained, which is apt to retain traces of the dichloride, and can only be purified by repeated distillation at about 140° F. This chloride is a liquid of a deep reddish-brown tint, and has a density of 1.62. It boils at 147°, and the density of its vapour is between 3.67 and 3.70. By decomposition in water, it should yield hydrochloric and hyposulphurous acids. (An. de Ch. et de Ph. xlix. 205.)

Perchloride of Phosphorus.—There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Davy. (Elements, p. 290.) When phosphorus is introduced into a jar of dry chlorine, it inflames, and on the inside of the vessel a white matter collects, which is *perchloride of phosphorus.* It is very volatile, a temperature much below 212° being sufficient to convert it into vapour. Under pressure it may be fused, and it yields transparent prismatic crystals in cooling.

Water and perchloride of phosphorus mutually decompose each other; and the sole products are hydrochloric and phosphoric acids. Now in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 200, the perchloride must consist of 31.4 parts or two equivalents of phosphorus, and 177.1 parts or five eq. of chlorine. One equivalent of the chloride and five eq. of water will then mutually decompose each other without any element being in excess, and yield one eq. of phosphoric, and five eq. of hydrochloric acid. This proportion is not far from the truth; for according to Davy, one grain of phosphorus is united in the perchloride with six of chlorine.

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* Nicholson's Journal vol. vi.

† Mémoires d'Arcueil, vol. i.

Sesquichloride of Phosphorus may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid like water, of specific gravity 1.45; emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water, mutual decomposition ensues, heat is evolved, and a solution of hydrochloric and phosphorous acids is obtained. It hence appears to consist of 31.4 parts or two equivalents of phosphorus, and 106.26 parts or three eq. of chlorine.

When hydrosulphuric acid gas is transmitted through a vessel containing perchloride of phosphorus, hydrochloric acid is disengaged, and a liquid produced which, according to Serullas, is a compound of three equivalents of chlorine, one of phosphorus, and one of sulphur. (An. de Ch. et de Ph. xlii. 25.)

Chlorocarbonic Acid Gas.—This compound was discovered in 1812 by Dr. Davy, who described it in the Philosophical Transactions for that year under the name of *phosgene gas.* (From φως light, and γενναν to produce.) It is made by exposing a mixture of equal measures of dry chlorine and carbonic oxide gases to sunshine, when rapid but silent combination ensues, and they contract to one-half their volume. Diffused daylight also effects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

Chlorocarbonic acid gas is colourless, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One equivalent of each compound undergoes decomposition; and as the hydrogen of the water unites with chlorine, and its oxygen with carbonic oxide, the products are carbonic and hydrochloric acids. When tin is heated in this gas, chloride of tin is generated, and carbonic oxide gas set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc, or arsenic.

As chlorocarbonic acid gas contains its own volume of each of its constituents, it follows that 100 cubic inches of that gas at the standard temperature and pressure must weigh 106.7638 grains; namely, 76.5988 of chlorine added to 30.1650 of carbonic oxide. Its specific gravity is, therefore, 3.4427, and it consists of 35.42 parts or one equivalent of chlorine, and 14.12 parts or one equivalent of carbonic oxide.

Chloral.—This name, derived from the first syllable of the words *chlorine* and *alcohol*, has been applied by Liebig to a new compound of chlorine, carbon, and oxygen, prepared by the mutual action of alcohol and chlorine. The production of the new substance more immediately depends on the union of one portion of chlorine with the hydrogen both of the olefiant gas and some of the water which constitute alcohol, while the corresponding carbon and oxygen unite with another portion of chlorine. A very large quantity of chlorine is, therefore, required for its production, and a large quantity of hydrochloric acid is generated. When chlorine is transmitted through common alcohol, the chloral at first formed is retained in solution by the water of the alcohol; but when the liquid becomes charged with hydrochloric acid, the chloral insoluble in that solution subsides as a liquid of an oily aspect. The method recommended by Liebig is to transmit dry chlorine gas into absolute alcohol. At first the alcohol should be artificially cooled, since otherwise the action is attended with flame; but as soon as hydrochloric acid begins to accumulate, it is necessary to expel it by a continued gentle heat, since its presence protects the alcohol from decomposition, and thereby prevents the absorption of the chlorine. By acting in this manner for several successive days, Liebig succeeded in decomposing eight ounces of absolute alcohol, and obtained a liquid of syrupy consistence, which after a few days became a soft white crystalline solid. In this state the chloral is united with water as a hydrate of unknown composition, and also contains traces of undecomposed alcohol and hydrochloric acid. On agitation with strong sulphuric acid, it is rendered anhydrous, and rises as a liquid to the surface; and by distillation from unslaked lime or baryta, it is entirely separated from hydrochloric acid.

Pure chloral is a colourless transparent liquid of a penetrating pungent odour, is oily to the touch, and has a density of 1.502. It is nearly tasteless, or at most oily. It boils at 201°, and may be distilled without change. In water, with the aid of gentle heat, it is freely dissolved without decomposition. Agitated with a few drops of water, it forms a white crystalline mass which appears to be a hydrate, though its composition is unknown; for when put into water, the chloral appears oily as usual, and by heat a solution having the characteristic odour and character of chloral is obtained. On keeping this crystalline hydrate for a few days, it becomes a very white flocculent matter, which is quite insoluble in water. From the ratio of its ingredients Liebig regards it also as a hydrate, formed of two equivalents of water to one of chloral.

Chloral unites with iodine, bromine, and sulphur. It may be distilled from the anhydrous metallic oxides without change; but when its vapour is transmitted over anhydrous baryta, strontia, or lime, heated to 212°, instant decomposition ensues and the earth becomes incandescent. Carbonic oxide gas escapes at the same time, and a metallic chloride, intermixed with a light charcoal, is generated. Similar products are obtained, but of course more charcoal, when the vapour of chloral is transmitted over iron or copper at a red heat. Chloral is readily decomposed by the alkalies or alkaline earths in the state of hydrates or when dissolved in water, giving rise to a chloride of carbon, as already described. (An. de. Ch. et de Ph. xlix. 146.)

Terchloride of Boron.—Sir H. Davy noticed that recently prepared boron takes fire spontaneously in an atmosphere of chlorine, and emits a vivid light; but he did not examine the product. Berzelius remarked, that if the boron has been previously heated, whereby it is rendered more compact, the combustion does not take place till heat is applied. This observation led him to expose boron, thus rendered dense, in a glass tube to a current of dry chlorine; and to heat it gently as soon as the atmospheric air was completely expelled, in order to commence the combustion. The resulting compound proved to be a colourless gas; and on collecting it over mercury, which absorbed free chlorine, he procured the chloride of boron in a state of purity. This gas is rapidly absorbed by water; but double decomposition takes place at the same instant, giving rise to hydrochloric and boracic acids as the sole products: from this fact is inferred the composition of the chloride as stated at page 212; for one eq. of terchloride of boron or $B + 3Cl$, and three eq. of water or $3\,(H + O)$, correspond to one eq. of boracic acid or $B + 3O$, and three eq. of hydrochloric acid or $3(H + Cl)$. The watery vapour of the atmosphere occasions a similar change; so that when the gas is mixed with air containing hygrometric moisture, a dense white cloud is produced. The specific gravity of the gas, according to Dumas, is 3.942. It is soluble in alcohol, and communicates to it an ethereal odour, apparently by the action of hydrochloric acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown.—(Annals of Phil. xxvi. 129.)

Dumas finds that chloride of boron may be generated by the action of dry chlorine on a mixture of charcoal and boracic acid, heated to redness in a porcelain tube. Despretz also appears to have invented a similar process. (Philos. Magazine and Annals, i. 469.)

Chloro-nitrous Gas.—When fused chloride of sodium, potassium, or calcium, in powder, is treated with as much strong nitric acid as is sufficient to wet it, mutual decomposition ensues, and a new gas, composed of chlorine and binoxide of nitrogen, is generated. Its discoverer, Mr. E. Davy, describes it as a gas of a pale reddish-yellow colour, of an odour similar to that of chlorine, though less pungent, and possessed of bleaching properties.

It fumes on exposure to the air, and is freely absorbed by water. It is decomposed by sulphur, phosphorus, mercury, and most metals, and by substances in general which have an affinity for chlorine. It consists, according to Mr. Davy, of equal volumes of chlorine and binoxide of nitrogen, united without any condensation.

In the mutual decomposition of chloride of sodium and nitric acid, the products appear to be chloro-nitrous and chlorine gases, and nitrate of soda. Their formation must obviously depend on sodium being oxidized at the expense of nitric acid; while part of the chlorine unites, at the moment of separation from the sodium, with binoxide of nitrogen. (Phil. Mag. ix. 355.) Theoretically, it should be mixed with twice its volume of chlorine, the presence of which must materially obscure the properties of the new gas.

ON THE NATURE OF CHLORINE.

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily, and in a manner so consistent with the received chemical doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place; and this hypothesis, though it has not hitherto been rigidly demonstrated to be erroneous, has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing it with the opposite theory, and examining the evidence in favour of each.

Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple, because it has not hitherto been decomposed; but as chemists have no other mode of estimating the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Hydrochloric acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when exposed to the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, hydrochloric acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. According to that view, hydrochloric acid gas is composed of *absolute muriatic acid* and water or its elements; chlorine consists of *absolute muriatic acid* and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, hydrochloric acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to elicit from that gas a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and, therefore, its supposed base is also imaginary.

But this is not the only weak point of the doctrine. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. For instance, on exposing chlorine to a powerful galvanic battery, oxygen gas does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and, therefore, cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as nitric and oxalic acids, which appear to be incapable of existing except when combined with water or some other substance. The analogy, however, is incomplete; for the decomposition of such compounds, when an attempt is made to procure them in an insulated state, is manifestly owing to the tendency of their elements to enter into new combinations.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as by the new theory. Thus, when hydrochloric acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that *absolute muriatic acid* attaches itself to the oxygen of the water, and forms chlorine; while the hydrogen of the water goes to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter; and that hydrochloric acid gas is generated by the water so formed combining with the *absolute muriatic acid* of the chlorine. The evolution of chlorine, which ensues on mixing hydrochloric acid and peroxide of manganese, is explained on the supposition that *absolute muriatic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult, after these observations, to account for the preference shown to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science; for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general.

It was supposed, indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with some simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing, therefore, can be gained, much may be lost by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the same opinion, though in direct opposition to the result of observation, ought to be extended to iodine and bromine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr. Murray, to demonstrate the presence of water or its elements as a constituent part of hydrochloric acid gas, and thus to establish the old theory to the subversion of the new. The arguments which he used, though plausible and ingenious, were successfully combated by Sir H. and Dr. Davy. The only experiment which strictly bears upon the question,—that, namely, where hydrochloric acid and ammoniacal gases were mixed together, goes far to demonstrate the absence of combined water in hydrochloric acid gas, and thereby to establish the views of Davy.*

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* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

SECTION XII.

IODINE.

Iodine was discovered in the year 1812 by M. Courtois, a manufacturer of salt-petre at Paris. In preparing carbonate of soda from the ashes of sea-weeds, he observed that the residual liquor corroded metallic vessels powerfully; and on investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark-coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clément, who recognized it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine.*

Iodine is frequently met with in nature in combination with potassium or sodium. Under this form it occurs in many salt and other mineral springs, both in England and on the continent. It has been detected in the water of the Mediterranean, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Dr. Fyfe (Edin. Philos. Journal, i. 254.) may be separated by the action of water; but in others it can be detected only after incineration. Marine animals and plants doubtless derive from the sea the iodine which they contain. Vauquelin found it also in the mineral kingdom, in combination with silver. (An. de Ch. et de Ph. xxix.)

All the iodine of commerce is procured from the impure carbonate of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, by incinerating sea-weeds. The kelp is employed by soap-makers, for the preparation of carbonate of soda; and the dark residual liquor, remaining after that salt has crystallized, contains a considerable quantity of iodine, combined with sodium or potassium. By adding a sufficient quantity of sulphuric acid, hydriodic acid is first generated, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add to the mixture some peroxide of manganese, which acts on hydriodic in the same way as on hydrochloric acid (page 209), (Phil. Mag. L. Dr. Ure.) Another method proposed by Soubeiran, is by adding to the ley from kelp a solution made with the sulphates of protoxides of copper and iron in the ratio of 1 of the former to 2¼ of the latter, as long as a white precipitate appears. The diniodide of copper is thus thrown down; and it may be decomposed either by peroxide of manganese alone, or by manganese and sulphuric acid. By means of the former, the iodine passes over quite dry; but a strong heat is requisite.

Iodine, at common temperatures, is a soft friable opaque solid of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is a rhombic octohedron. The crystals are best prepared by exposing to the air a solution of iodine in hydriodic acid. Its specific gravity, according to Gay-Lussac, is 4.948; but Dr. Thomson found it only 3.0844. At 225° it is fused, and enters into ebullition at 347°; but when moisture is present, it is sublimed rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *iodine*. (From ἰώδης, violet-coloured.) This vapour is remarkably dense, its specific gravity by calculation, page 146, being 8.7020, or 8.716 as directly observed by Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 269.8638 grains.

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* The original papers on this subject are in the Annales de Chimie, vols. lxxxviii. xc. and xci.; and in the Philos. Trans. for 1814 and 1815.

Iodine is a non-conductor of electricity, and, like oxygen and chlorine, is a negative electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed medicinally in very small doses with advantage.

Iodine is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances, producing compounds which are termed *iodides* or *iodurets*. It is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it in the same manner as upon chlorine, giving rise to decomposition of water, and the formation of an iodate and iodide.

Pure iodine is not influenced chemically by the imponderables. Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in cold water, which is recognized with certainty by its deep blue colour. This test, according to Stromeyer, is so delicate, that a liquid, containing 1—450,000 of its weight of iodine, receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unites with starch. Secondly, the solution should be quite cold at the time of adding the starch; for hot water dissolves the blue compound, and forms a colourless solution.

Berzelius determined the equivalent of iodine by exposing fused iodide of silver to a current of chlorine gas, whereby the iodine was expelled and chloride of silver generated. Through the known composition of chloride of silver he inferred that of the iodide, and thence found that the equivalent of iodine is 126.3.

The composition of the compounds of iodine described in this section is as follows:—

	Iodine.			Equiv.	Formulæ.
Hydriodic acid	126.3	1 eq. + 1	1 eq. hydrogen	=127.3.	$H+I$ or HI.
Oxide of iodine Iodous acid	Composition unknown.				
Iodic acid	126.3	1 eq. + 40	5 eq. oxygen	=166.3.	$I+5O$ or $\overset{\cdot\cdot\cdot\cdot\cdot}{I}$.
Periodic acid	126.3	1 eq. + 56	7 eq. ditto	=182.3.	$I+7O$ or $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{I}$.
Chlorides of iodine	Composition unknown.				

	Iodine.					Equiv.	Formulæ.
Teriodide of nitrogen	378.9	3 eq.	+ 14.15	1 eq.	nitrogen	= 393.05.	N + 31 or NI^3.
Protiodide of phos.	126.3	1 eq.	+ 15.7	1 eq.	phosph.	= 142.0.	P + I or PI.
Sesquiodide of phos.	378.9	3 eq.	+ 31.4	2 eq.	do.	= 410.3.	2P + 3I or P^2I^3.
Periodide of phos.	631.5	5 eq.	+ 31.4	2 eq.	do.	= 662.9.	2P + 5I or P^2I^5.
Iodide of sulphur	Composition unknown.						
Periodide of carbon	Composition unknown.						
Protiodide of carbon	Composition unknown.						

Hydriodic acid.—This compound is formed by the direct union of its elements, when a mixture of hydrogen gas and iodine vapour are transmitted through a porcelain tube at a red heat. A more convenient process, and by which it is obtained in a pure state, is by the action of water on the periodide of phosphorus. Any convenient quantity of the iodide is put into a small glass retort, together with a little water, and a gentle heat is applied. Mutual decomposition ensues; the oxygen of the water unites with phosphorus, and its hydrogen with iodine, giving rise to the formation of phosphoric and hydriodic acids, the latter of which passes over in the form of a colourless gas. The preparation of the iodide requires care; since phosphorus and iodine act so energetically on each other by mere contact, that the phosphorus is generally inflamed, and a great part of the iodine expelled in the form of vapour. This inconvenience is avoided by putting the phosphorus into a tube, sealed at one end and about twelve inches long, displacing the air by a current of dry carbonic acid gas, then gradually adding the iodine, and promoting the action towards the close by a gentle heat. The materials should be well dried with bibulous paper, and the iodide preserved in a well stopped dry vessel; for even atmospheric humidity gives rise to copious white fumes of hydriodic acid. The proportions usually employed are one part of phosphorus to about twelve of iodine.

Another process has been recommended by M. F. d'Arcet, which consists in evaporating hypophosphorous acid until it begins to yield phosphuretted hydrogen, mixing it with an equal weight of iodine, and applying a gentle heat. Hydriodic acid gas of great purity is then rapidly disengaged; its production depending, as in the former process, on the decomposition of water.

Hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, produces dense white fumes when mixed with atmospheric air, and has an odour similar to that of hydrochloric acid gas. The salts which it forms with alkalies are called *hydriodates*. Like hydrochloric acid gas, it cannot be collected over water; for that liquid dissolves it in large quantity.

Hydriodic acid is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with its hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; hydrochloric acid gas is produced, and the iodine appears in the form of vapour. With strong nitrous acid it takes fire, and the vapour of iodine is set free. It is also decomposed by mercury. The decomposition begins as soon as hydriodic acid gas comes in contact with mercury, and proceeds steadily, and even quickly if the gas is agitated, till nothing but hydrogen remains. Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. Assuming it to consist of equal volumes of hydrogen gas and iodine vapour united without any condensation, then, since

	Grains.
50 cubic inches of the vapour of iodine weigh .	134.9319
50 do. hydrogen gas	1.0683
100 cubic inches of hydriodic acid gas should weigh	136.0002

These numbers are obviously in the ratio of 1 to 126.3, the equivalents of iodine and hydrogen. On the same principles the density of the gas should be 4.3854, which is probably more correct than 4.443, a number found experimentally by Gay-Lussac. (An. de Ch. xci. 16.) From these coincidences there is no doubt that 100 measures of hydriodic acid gas contain 50 measures of hydrogen gas and 50 of the vapour of iodine.

When hydriodic acid gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a density of 1.7. It may be prepared also by transmitting a current of hydrosulphuric acid gas through water in which iodine in fine powder is suspended. The iodine, from having a greater affinity than sulphur for hydrogen, decomposes the hydrosulphuric acid; and hence sulphur is set free, and hydriodic acid produced. As soon as the iodine has disappeared, and become colourless, it is heated for a short time to expel the excess of hydrosulphuric acid, and subsequently filtered to separate free sulphur.

The solution of hydriodic acid is readily decomposed. Thus, on exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a yellow tint from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. Nitric and sulphuric acids likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and hydrochloric acid is formed. The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that is necessary, is to mix a cold solution of starch with the liquid, previously concentrated by evaporation if necessary, and then add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Oxide of Iodine and Iodous Acid.—M. Sementini, of Naples, states that on mixing the vapour of iodine and oxygen gas considerably heated, the violet tint of the former disappears, and a yellow matter of the consistence of solid oil is generated. This he regards as oxide of iodine; and if the supply of oxygen be kept up after its formation, it is converted into a yellow liquid, which he supposes to be iodous acid. From the mode in which the process is described, there can scarcely be a doubt that some compound of iodine and oxygen is thus formed; but its composition and properties have not been satisfactorily made out. (Quarterly Journ. of Science, N. S. i. 478.)

Mitscherlich has observed, that on dissolving iodine in a rather dilute solution of soda, until the solution began to acquire a red tint, permanent crystals were obtained by spontaneous evaporation. They had the form of a six-sided prism, and dissolved in cold water without change; but by the action of water moderately heated, or by alcohol, they were converted into iodate of soda and iodide of sodium. On the addition of an acid, iodine and iodic acid were set at liberty. From these facts the crystals were inferred to be iodite of soda. (An. de Ch. et de Ph. xxx. 84.)

Iodic Acid.—This acid was discovered at about the same time by Gay-Lussac and Davy; but the latter first succeeded in obtaining it in a state of perfect purity. When iodine is brought into contact with protoxide of chlorine, immediate action ensues; the chlorine of the protoxide unites with one portion of iodine, and its oxygen with another, forming two compounds, a volatile orange-coloured matter, chloride of iodine, and a white solid substance, which is *iodic acid.* On applying heat, the former passes off in vapour, and the latter remains. (Philos. Trans. for 1815.) Serullas has obtained it, in the form of hexagonal laminæ, by evaporating in a warm place its solution either in water, or in sulphuric or nitric acid. The method which he found most convenient is by forming a solution of iodate of soda in a considerable excess of sulphuric acid, keeping it at a boiling temperature for twelve or fifteen minutes, and then setting it aside to crystallize. (An. de Ch. et de Ph. xliii. 216.) Iodic acid may also be formed by dissolving perchloride of iodine in water, and gradually adding a large quantity of strong sulphuric acid, a rise of temperature being at the same time prevented by the application of cold. Iodic acid will then be precipitated. Another process, suggested by Mr. Connell of Edinburgh, is by boiling iodine in nitric acid. For this purpose a pure acid of density 1.5 should be introduced along with about a fifth of its weight of iodine into a tube sealed at one end, about an inch wide and 15 inches long, and these materials be kept at a boiling temperature for at least twelve hours. As the iodine rises and condenses on the sides of the tube, it should be restored to the liquid, either by agitation or by help of a glass rod. As soon as the iodine disappears, the nitric acid is dissipated by cautious evaporation.

This compound, which was termed *oxiodine* by Davy, is *anhydrous iodic acid*. It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its density is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F. it is fused, and at the same time resolved into oxygen and iodine. In a dry air it is unchanged; but in a moist atmosphere it absorbs humidity, forming the hydrated acid, and eventually deliquesces. In water it is very soluble, and the solution has a distinct acid reaction: the bleaching power ascribed to it by Davy is said by Mr. Hiley not to be a property of pure iodic acid. (Lancet for July 1833.) On evaporating the solution, a thick mass of the consistence of paste is left, which is hydrous iodic acid; and which, by the cautious application of heat, may be rendered anhydrous. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar, and similar combustibles, it forms mixtures which detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates*. These compounds, like the chlorates, yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid forms with the pure alkalies, salts which are soluble in water; but with lime, baryta, strontia, and the oxides of lead and silver, it yields compounds of very sparing solubility. It is readily detected by the facility with which it is deoxidized, an effect readily produced by the sulphurous, phosphorous, hydriodic, and hydrosulphuric acids. Iodine in each case is set at liberty, and may be detected as usual by starch. Hydrochloric and iodic acids decompose each other, water and chloride of iodine being generated.

Davy ascertained the composition of iodic acid, as given at page 227, by determining the quantity of oxygen which the acid loses when decomposed by heat; and Gay-Lussac arrived at the same result by heating iodate of potassa, when pure oxygen was given off and iodide of potassium remained.

Periodic Acid.—This compound has been lately discovered by Ammermüller and Magnus. (Poggen. Annalen, xxviii. 514.) When pure soda is mixed with a solution of iodate of soda, and chlorine gas is transmitted into it to saturation, a sparingly soluble white pulverulent salt is generated, which subsides after heating, and, if necessary, concentrating the solution. This salt is periodate of soda, the production of which appears to depend on the formation of chloride of sodium, and the union of the oxygen of the soda with the iodine of the iodic acid. For each equivalent of periodic acid, two eq. of chloride of sodium should be generated; since the materials $I + 5O$, $2(Na + O)$, $2\,Cl$, just suffice for yielding $I + 7O$, and $2(Na + Cl)$. On dissolving the periodate of soda in dilute nitric acid, and adding nitrate of oxide of silver, the periodate of this oxide, of a greenish-yellow colour, subsides, which should be washed with water acidulated with nitric acid. This yellow salt is soluble in hot dilute nitric acid, and separates again on cooling in small shining straw-yellow crystals, which by digestion with warm water acquire, without dissolving, a reddish-brown almost black colour. If the nitric acid solution of the yellow salt is so far concentrated by evaporation, that it crystallizes while still warm, orange-coloured crystals subside. These three salts are readily analyzed by exposure to a red heat in a glass tube, when iodine and metallic silver remain in the tube, and oxygen gas, along with water when water is present, is expelled. Their composition is as follows:—

	Oxide of Silver.		Periodic Acid.		Water.		Formulæ.
Yellow salt	232	2 eq.	182.3	1 eq.	27	3 eq.	$\dot{\mathrm{Ag}}^{2}\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\mathrm{I}}+3\dot{\mathrm{H}}$.
Red salt	232	2 eq.	182.3	1 eq.	18	2 eq.	$\dot{\mathrm{Ag}}^{2}\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\mathrm{I}}+2\dot{\mathrm{H}}$.
Orange salt	116	1 eq.	182.3	1 eq.			$\dot{\mathrm{Ag}}\,\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\mathrm{I}}$.

The two former are, therefore, hydrated subperiodates of oxide of silver, and the latter a neutral periodate. This neutral salt has the peculiarity, that by pure cold water it is converted into the yellow subsalt, while the water takes up exactly half of its acid without a trace of silver. By this means a pure solution of periodic acid may be obtained.

Periodic acid is analogous in composition to perchloric acid, and has decided acid properties. Its solution may be boiled without decomposition, and on evaporation the acid yields crystals, which do not change by exposure to the air. By hydrochloric acid it is reduced to iodic acid with disengagement of chlorine, and the same change will of course be produced by substances which decompose iodic acid. When the heat is increased beyond 212° (the precise point is not stated) periodic acid loses oxygen, and iodic acid remains. Thus is periodic more easy of decomposition than iodic acid.

Chlorides of Iodine.—Chlorine is absorbed at common temperatures by dry iodine with evolution of heat, and a solid compound of iodine and chlorine results, which was discovered both by Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if iodine is in excess. It is converted by heat into an orange-coloured liquid, which yields a vapour of the same tint on increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution is colourless, very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Davy gave it the name of *chloriodic acid*. Gay-Lussac, on the contrary, calls it *chloride of iodine*, conceiving that the acidity of its solution arises from the presence of hydrochloric and iodic acids, which he supposes to be generated by decomposition of water. From the observations of Serullas and Dumas, it appears that there exist two compounds of chlorine and iodine, by the different action of which on water the discordant opinions of Davy and Gay-Lussac may be explained. The chloride is soluble in water, alcohol, and ether without change; but the perchloride is resolved by water into hydrochloric and iodic acids, the latter of which may be precipitated either by rectified alcohol or strong sulphuric acid. The substance commonly obtained by transmitting chlorine gas over iodine is a mixture of the two chlorides; and on dissolving it in water, and agitating with ether, the undecomposed chloride is removed by the ether, while the iodic acid of the decomposed perchloride is precipitated. The composition of these chlorides has not been precisely determined. They are both converted by alkaline solutions into hydrochloric and iodic acids.

Teriodide of Nitrogen.—From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodine, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterized, like quadrochloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried; and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and, iodine and nitrogen are set free. According to the experiments of M. Colin, iodide of nitrogen consists of one equivalent of nitrogen and three of iodine.

It is conveniently made, according to Serullas, by saturating alcohol of 0.852 with iodine, adding a large quantity of pure ammonia, and agitating the mixture. On diluting with water, teriodide of nitrogen subsides, which should be washed by repeated affusion of water and decantation. As thus prepared it is very finely divided, and may be pressed under water without detonating; but if, subsequently to its formation, it is put in contact with pure ammonia, it will afterwards detonate with the same facility as that prepared in the usual manner.

Serullas has also remarked that water and teriodide of nitrogen mutually decompose each other, giving rise to the formation of hydriodic and iodic acids and ammonia. The change takes place slowly in cold water; but it is completed in a few minutes, and with scarcely any disengagement of nitrogen, when gentle heat is applied. When a little nitric or sulphuric acid is used, ammonia and iodic acid are alone produced. (An. de Ch. et de Ph. xlii. 201.)

Iodides of Phosphorus.—Iodine and phosphorus combine readily in the cold, evolving so much heat as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. One of these compounds, apparently a protiodide, is formed of 1 part of phosphorus and 7 or 8 parts of iodine. It has an orange colour, fuses at 212°, sublimes unchanged by heat, and is decomposed by water, with the elements of which it gives rise to hydriodic and phosphorous acids, while phosphorus is set free.

The sesquiodide is formed by the action of 1 part of phosphorus and 12 of iodine. It appears as a dark gray crystalline mass, fusible at 84°, and yields with water hydriodic and phosphorous acids, from which circumstance its elements are supposed to be in the ratio of two eq. of phosphorus to three eq. of iodine.

The periodide is prepared with 1 part of phosphorus and 20 of iodine, and is a black compound, fusible at 114°. As by the action of water it yields hydriodic and phosphoric acids only, it is inferred to contain phosphorus and iodine in the ratio of two eq. to five eq. Thus

1 eq. periodide phos, & 5 eq. water yield 1 eq. phos. acid & 5 eq. hydriodic acid.
$2P+5I$ $\quad$ $5(H+O)$ $\quad$ $2P+5O$ $\quad$ $5(H+I)$

Iodide of Sulphur.—This compound is formed by heating gently 4 parts of iodine with 1 of sulphur. The product has a dark colour and radiated appearance like antimony. Its elements are easily disunited by heat.

Periodide of Carbon.—When a solution of pure potassa in alcohol is mixed with an alcoholic solution of iodine, a portion of alcohol is decomposed; and its hydrogen and carbon, uniting separately with iodine, give rise to periodide of carbon and hydriodic acid. The latter combines with the potassa, and remains in solution. The former has a yellow colour like sulphur, and forms scaly crystals of a pearly lustre; its taste is very sweet, and it has a strong aromatic odour resembling saffron. It was discovered by Serullas, and described by him as a hydrocarburet of iodine; but its real nature was pointed out by Mitscherlich. An. de Ch. de Ph. xxxvii. 86.)

The protiodide is formed by distilling a mixture of the preceding compound with corrosive sublimate. It is a liquid of a sweet taste, and has a penetrating ethereal odour.

SECTION XIII.

BROMINE.

Bromine was discovered in 1826 by M. Balard of Montpellier. The name originally applied to it was *muride*, but the term *brome* or *bromine*, from *βρωμος graveolentia*, signifying a strong or rank odour, has since been substituted. (An. of Phil. xviii. 381.)

Bromine in its chemical relations bears a close analogy to chlorine and iodine, and has hitherto been always found in nature associated with the former, and sometimes also with the latter. It exists in sea-water in the form of bromide of sodium or magnesium. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern*, left after chloride of sodium has been separated from sea-water by crystallization, contains it in small proportion. It may apparently be regarded as an essential ingredient of the saline matter of the ocean; for it has been detected in the waters of the Mediterranean, Baltic, North Sea, and Frith of Forth. It has also been found in the waters of the Dead Sea, and in a variety of salt springs in Germany.* Dr. Daubeny has detected it in several mineral springs in England; and states that it is rarely wanting in those springs which contain much common salt, except that of Droitwich in Worcestershire. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and has procured it in appreciable quantity from the ashes of sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light, but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable, and its taste powerful. Its specific gravity is about 3. Its volatility is considerable: for at common temperatures it emits red-coloured vapours which are very similar in appearance to those of nitrous acid; and at 116.5° it enters into ebullition. By a temperature between zero and —4° it is congealed, and in that state is brittle. The density was found by Mitscherlich to be 5.54, and the number calculated (page 146) from its equivalent is 5.4017; 100 cubic inches at 60° and 30 inches Bar. should weigh 167.5158 grains.

Bromine is a non-conductor of electricity, and undergoes no chemical change whatever from the agency of the imponderables. It may be transmitted through a red-hot glass tube, and be exposed to the agency of galvanism, without evincing the least trace of decomposition. Like oxygen, chlorine, and iodine, it is a negative electric. Bromine is soluble in water, alcohol, and ether, the latter being its best solvent. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo. Its vapour extinguishes a lighted taper; but before going out, it burns for a few seconds with a flame which is green at its base and red at its upper part. Some inflammable substances take fire by contact with bromine, in the same manner as when introduced into an atmosphere of chlorine. It acts with energy on organic matters such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. To animal life it is highly destructive, one drop of it placed on the beak of a bird having proved fatal.

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* Some of the salt springs of Germany furnish a good deal of bromine. The saline at Theodorshalle, near Kreuznach, contains a sufficient quantity to make its extraction profitable. A quintal (100 lbs.) of the mother-waters of this spring yields two ounces and one drachm of bromine.—*Berzelius, Traité de Chimie*, i. 293.—*Ed.*

From the close resemblance observable between chlorine and bromine, Balard was of course led to examine its relations with hydrogen, and found that these substances may readily be made to unite; the product of the combination being a gas very similar to hydrochloric and hydriodic acid gases, whence it has received the name of *hydrobromic* acid gas. In its action on metals, also, bromine presents the closest similarity to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense heat as to cause a vivid flash of light, and often to burst the vessel in which the experiment is performed. Its affinity for metallic oxides is feeble. By the action of alkalies it is resolved into hydrobromic and bromic acids, suffering the same kind of change as chlorine or iodine, when similarly treated.

Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydrobromic acid, uniting with its hydrogen, and setting bromine at liberty. Accordingly, on adding chlorine to bittern, the free bromine immediately communicates an orange-yellow tint to that liquid; and on heating the solution to its boiling point, the red vapours of bromine are expelled, and may be condensed by being conducted into a tube surrounded with ice. It was this change of colour produced by chlorine that led to the discovery of bromine. The method recommended by Balard for procuring this substance as well as for detecting the presence of hydrobromic acid, is to transmit a current of chlorine gas through bittern, and then to agitate a portion of sulphuric ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth-red tint, and on standing it rises to the surface. When the ethereal solution is agitated with caustic potassa, its colour entirely disappears, owing to the formation of bromide of potassium and bromate of potassa, the former of which is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, and separated by heat.* Balard has subsequently improved the process so much, that it is now produced in considerable quantity, and sold in Paris as an article of commerce.

According to all the experiments hitherto made, bromine appears to be an element. It is so very similar in most aspects to chlorine and iodine, and, in the order of its chemical relations, is so constantly intermediate between them, that Balard at first supposed it to be some unknown compound of these substances. There seems, however, to be no good ground for the supposition; but on the contrary, an experiment performed by De la Rive affords a very strong argument against it. He finds that when a compound of bromine and iodine is mixed with starch, and exposed to the influence of galvanism, bromine appears at the positive and iodine at the negative wire, where the starch acquires a blue tint. On making the experiment with bromine containing a little bromide of iodine, the same appearance ensues; but if iodine is not previously added, the starch does not receive a tint of blue.

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* According to the authorities of Berzelius and Thenard, the best mode of treating the cubic crystals of bromide of potassium in order to extract the bromine, is to mix them in a small retort with the peroxide of manganese in powder, and to act on the mixture with sulphuric acid, diluted with half its weight of water, with the assistance of heat. The beak of the retort must plunge under cold water. As the distillation proceeds, the bromine passes over in red vapours, and condenses under the water in the form of brown and heavy drops.—*Berzelius*, *Traité de Chim.* i. 293.—*Ed.*

Bromine is in most cases easily detected by means of chlorine; for this substance displaces bromine from its combination with hydrogen, metals, and most other bodies. The appearance of its vapour or the colour of its solution in ether will then render its presence obvious.

Bromine, like chlorine, forms a crystalline hydrate when exposed to 32° F. in contact with water. The crystals are octohedral, of a beautiful red tint, and suffer decomposition at 54°. (Lowig.)

Berzelius determined the equivalent of bromine in the same way as that of iodine, namely, by heating a known weight of bromide of silver in a current of chlorine gas, so as to displace the bromine and obtain chloride of silver. He thus found 78.4 to be the equivalent of bromine.

The compounds of bromine described in this section are as follows:—

	Bromine.				Equiv.	Formulæ.
Hydrobromic acid	78.4	1 eq.+Hydrogen	1	1 eq.=	79.4.	H+Br.
Bromic acid	78.4	1 eq.+Oxygen	40	5 eq.=	118.4.	Br+5O or $\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{Br}}$.
Chloride of bromine	Composition uncertain.					
Bromides of iodine	Composition uncertain.					
Bromide of sulphur	Composition uncertain.					
Protobromide of phos.	78.4	1 eq.+Phosph.	15.7	1 eq.=	94.1	P+Br.
Perbromide of phos.	392	5 eq.+ do.	31.4	2 eq.=	423.4	$P^2\,Br^5$.
Bromide of carbon	Composition uncertain.					

Hydrobromic Acid.—No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays; but on introducing a lighted candle, or a piece of red-hot iron, into the mixture, combination ensues in the vicinity of the heated body, though without extending to the whole mixture, and without explosion. The combination is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus on mixing the vapour of bromine with hydriodic acid, hydrosulphuric acid, or phosphuretted hydrogen gases, decomposition ensues, and hydrobromic acid gas is generated. It may be conveniently made for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields, by the aid of gentle heat, a large quantity of pure hydrobromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Hydrobromic acid gas is colourless, has an acid taste, and pungent odour. It irritates the glottis powerfully, so as to excite cough, and, when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by hydrochloric acid gas. It undergoes no decomposition when transmitted through a red-hot tube, either alone, or mixed with oxygen. It is not affected by iodine; but chlorine decomposes it instantly, with production of hydrochloric acid gas, and deposition of bromine. It may be preserved without change over mercury; but potassium and tin decompose it with facility, the former at common temperatures, and the latter by the aid of heat.

Hydrobromic acid gas is very soluble in water. The aqueous solution may be made by treating bromine with hydrosulphuric acid dissolved in water, or still better by transmitting a current of hydrobromic acid gas into pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydrobromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. Nitro-hydrobromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold.

The elements of sulphuric and hydrobromic acids react on each other in a slight degree; and hence, on decomposing bromide of potassium by sulphuric acid, the hydrobromic is generally mixed with a little sulphurous acid gas.

The composition of hydrobromic acid gas is easily inferred from the two following facts. 1. On decomposing hydrobromic acid gas by potassium, a quantity of hydrogen remains, precisely equal to half the volume of the gas employed; and, 2, when hydriodic acid gas is decomposed by bromine, the resulting hydrobromic acid occupies the very same space as the gas which is decomposed. Hence hydrobromic is analogous to hydriodic and hydrochloric acid gases, in containing equal measures of bromine vapour and hydrogen gas united without any change of volume; and since

			Grains.
50	cubic inches of	bromine vapour weigh	83.7579
50	do.	hydrogen gas	1.0683
100	do.	hydrobromic acid must weigh .	84.8262

These numbers are in the ratio of 1 to 78.4, which is the composition of the gas by weight. Its density is 2.7353.

Since bromine decomposes hydriodic, and chlorine hydrobromic acid, bromine, in relation to hydrogen, is intermediate between chlorine and iodine; for it has a stronger affinity for hydrogen than iodine, and a weaker than chlorine. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The salts of hydrobromic acid are termed *hydrobromates*. Like the free acid, they are decomposed, and the presence of bromine is detected, by means of chlorine. On mixing a soluble bromide with the nitrates of the protoxides of lead, silver, and mercury, white precipitates are obtained, which are very similar in appearance to the chlorides of those metals, but which are metallic bromides. On the addition of chlorine, the vapour of bromine is evolved.

Bromic Acid.—The only compound yet known of bromine and oxygen is that formed by the action of bromine on potassa, when a change exactly similar to that produced by chlorine (page 211) ensues, whereby bromide of potassium and bromate of potassa are generated; and the latter, being much less soluble than the former, is readily separated by evaporation. The bromate of the other alkalies and alkaline earths may be prepared in a similar manner.

The bromates are analogous to the chlorates and iodates. Thus bromate of potassa is converted by heat into bromide of potassium, with disengagement of pure oxygen gas, deflagrates like nitre when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as sulphurous and hydrosulphuric acids, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydrobromic and hydrochloric acids.

Bromate of potassa is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish-white with protonitrate of mercury; characters which, if true, serve as a good test to distinguish bromate from iodate and chlorate of potassa.

Bromic acid may be procured in a separate state by decomposing a dilute solution of bromate of baryta with sulphuric acid, so as to precipitate the whole of the baryta. The resulting solution of bromic acid may be concentrated by slow evaporation until it acquires the consistence of syrup; but on raising the temperature, in order to expel all the water, one part of the acid is volatilized, and the other resolved into oxygen and bromine. A similar result took place when the evaporation was conducted *in vacuo* with sulphuric acid; and accordingly all attempts to procure anhydrous bromic acid have hitherto failed.

Bromic acid has scarcely any odour, but its taste is very acid, though not at all corrosive. It reddens litmus paper powerfully at first, and soon after destroys its colour. It is not affected by nitric or sulphuric acid except when the latter is highly concentrated, in which case bromine is set free, and effervescence, probably owing to the escape of oxygen gas, ensues. From the analysis of bromate of potassa, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, it consists of one equivalent of bromine united with five of oxygen.

Chloride of Bromine.—This compound may be formed at common temperatures by transmitting a current of chlorine through bromine, and condensing the disengaged vapours by means of a freezing mixture. The resulting chloride is a volatile fluid of a reddish-yellow colour, much less intense than that of bromine; its odour is penetrating, and causes a discharge of tears from the eyes, and its taste very disagreeable. Its vapour is a deep yellow, like the oxide of chlorine, and it enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromides.

Chloride of bromine is soluble in water without decomposition; for the solution possesses the colour, odour, and bleaching properties of the compound, and discharges the colour of litmus paper without previously reddening it. By the action of the alkalies it is decomposed, being converted, by means of the elements of water, into hydrochloric and bromic acids.

Bromide of Iodine.—These substances act readily on each other, and appear capable of uniting in two proportions. The protobromide is a solid, convertible by heat into a reddish-brown vapour, which, in cooling, condenses into crystals of the same colour, and of a form resembling that of fern leaves. An additional quantity of bromine converts these crystals into a fluid, which in appearance is like a strong solution of iodine in hydriodic acid. This compound dissolves without decomposition in water, but with the alkalies yields hydrobromic and iodic acids.—The existence of two bromides of iodine can scarcely be regarded as satisfactorily established.

Bromide of Sulphur.—On pouring bromine on sublimed sulphur, combination ensues, and a fluid of an oily appearance and reddish tint is generated. In odour it somewhat resembles chloride of sulphur, and like that compound emits white vapours when exposed to the air; but its colour is deeper. It reddens litmus paper faintly when dry, but strongly if water is added. Cold water acts slowly upon bromide of sulphur; but at a boiling temperature the action is so violent that a slight detonation occurs, and three compounds, hydrobromic, hydrosulphuric, and sulphuric acids are formed. The formation of these substances is of course attributable to decomposition of water, and the union of its elements with bromine and sulphur. Bromide of sulphur is likewise decomposed by chlorine, which unites with sulphur and displaces bromine.

The composition of bromide of sulphur is unknown. It dissolves an excess both of chlorine and sulphur, and its elements separate from each other so readily, that it has hitherto been impracticable to procure a definite compound.

Bromides of Phosphorus.—When bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, they act suddenly on each other with evolution of heat and light, and two compounds are generated; one a crystalline solid, which is sublimed and collects in the upper part of the flask, and the other a fluid, which remains at the bottom. The former contains the most bromine, and the latter is supposed by Balard to consist of single equivalents of its elements.

The protobromide retains its liquid form even at 52° F. It is readily converted into vapour by heat, and on exposure to the air emits penetrating fumes. It reddens litmus paper faintly, an effect which is probably owing to the presence of moisture. With water it acts energetically and with free disengagement of heat, hydrobromic acid gas being evolved when only a few drops of water are employed; but if a large quantity is used, the gas is dissolved, and the acid solution leaves by evaporation a residuum, which burns slightly when dried, and is converted into phosphoric acid.

The perbromide is yellow in its solid state; but with gentle heat it becomes a red-coloured liquid, which by increase of temperature is converted into a vapour of the same tint. On cooling after fusion it yields rhombic crystals; but when its vapour is condensed, the crystals are acicular. It is decomposed by metals, probably with the formation of metallic bromides and phosphurets. It emits dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydrobromic and phosphoric acids. Hence its elements should be in the ratio of two eq. of phosphorus to five eq. of bromine.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromides with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but, on the contrary, bromine decomposes iodide of phosphorus.

Bromide of Carbon.—This compound is formed by the action of bromine on half its weight of periodide of carbon, when bromide of carbon and a subbromide of iodine are formed, the latter of which is removed by a solution of caustic potassa. At common temperatures it is liquid, but crystallizes at 32° F. Its taste is sweet, and it has a penetrating ethereal odour. It resembles protiodide of carbon in many respects; but is distinguished from it by the vapour which it emits on exposure to heat. (Serullas, in the An. de Ch. et de Ph. xxxix. 225.)

SECTION XIV.

FLUORINE.

THE substance to which this name is applied has not hitherto been obtained in an insulated form, and, therefore, the properties which are peculiar to it in that state are entirely unknown. From the nature of its compounds it appears to belong to the class of negative electrics, and like oxygen and chlorine to have a powerful affinity for hydrogen and metallic substances.

Berzelius determined the equivalent of fluorine, by finding that 100 parts of pure fluoride of calcium yield with sulphuric acid 175 parts of sulphate of lime. From these numbers fluoride of calcium is inferred to consist of 20.5 parts or one eq. of calcium, and 18.68 parts or one eq. of fluorine.

The compounds of fluorine described in this section are the following:—

	Fluorine.				Equiv.	Formulæ.
Hydrofluoric acid	18.68	1 eq.+Hydrogen	1		1 eq.=19.68	H+F or HF.
Fluoboric acid	56.04	3 eq.+Boron	10.9		1 eq.=66.94	B+3F or BF_3.

Hydrofluoric Acid.—This acid was first procured in its pure state in the year 1810 by Gay-Lussac and Thenard, and described in the second volume of their *Recherches Physico-Chimiques.* It is prepared by acting on the mineral called *fluor spar*, which is a fluoride of calcium, carefully separated from siliceous earth and reduced to fine powder, with twice its weight of concentrated sulphuric acid. The mixture is made in a leaden retort; and on applying heat, an acid and highly corrosive vapour distils over, which must be collected in a receiver of the same metal surrounded with ice. As the materials swell up considerably during the process, owing to a quantity of vapour forcing its way through a viscid mass, the retort should be capacious. At the close of the operation pure hydrofluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are precisely the same as in the formation of hydrochloric acid gas at page 213, fluorine being substituted for chlorine and calcium for sodium. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydrofluoric acid is anhydrous.

Hydrofluoric acid, at the temperature of 32° F, is a colourless fluid, and remains in that state at 59° if preserved in well stopped bottles; but when exposed to the air, it flies off in dense white fumes, which consist of the acid vapour combined with the moisture of the atmosphere. Its specific gravity is 1.0609; but its density may be increased to 1.25 by gradual additions of water. Its affinity for this liquid far exceeds that of the strongest sulphuric acid, and the combination is accompanied with a hissing noise, as when red-hot iron is quenched by immersion in water.

The vapour of hydrofluoric acid is much more pungent than chlorine or any of the irritating gases. Of all known substances, it is the most destructive to animal matter. When a drop of the concentrated acid of the size of a pin's head comes in contact with the skin, instantaneous disorganization ensues, and deep ulceration of a malignant character is produced. On this account the greatest care is requisite in its preparation.

This acid when concentrated acts energetically on glass. The transparency of the glass is instantly destroyed, heat is evolved, and the acid boils, and in a short time entirely disappears. A colourless gas, commonly known by the name of *fluosilicic acid gas*, is the sole product. This compound is always formed when hydrofluoric acid comes in contact with a siliceous substance. For this reason it cannot be preserved in glass; but must be prepared and kept in metallic vessels. Those of lead, from their cheapness, are often used; but vessels of silver or platinum are preferable. In consequence of its powerful affinity for siliceous matter, hydrofluoric acid may be employed for etching on glass; and when used with this intention, it should be diluted with three or four times its weight of water.

Hydrofluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and neutralizes alkalies, either forming salts termed *hydrofluates*, or most generally giving rise to metallic fluorides. All these compounds are decomposed by strong sulphuric acid with the aid of heat, and the hydrofluoric acid while escaping may be detected by its action on glass.

Hydrofluoric acid acts violently on some of the metals, especially on the bases of the alkalies. Thus when potassium is brought in contact with the concentrated acid, an explosion attended with heat and light ensues; hydrogen gas is disengaged, and a white compound, fluoride of potassium, is generated. It is a solvent for some elementary principles which resist the action even of nitro-hydrochloric acid. Thus it dissolves silicium, zirconium, and columbium, with evolution of hydrogen gas; and when mixed with nitric acid, it proves a solvent for silicium which has been condensed by heat, and for titanium. Nitro-hydrofluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or hydrochloric acid, are readily dissolved by hydrofluoric acid. As examples of this fact, several of the weaker acids, such as silica or silicic acid, titanic, columbic, molybdic, and tungstic acids may be enumerated. (Berzelius.)

A different view of the compounds of fluorine was originally taken by Gay-Lussac and Thenard, and is still held by some chemists. They adopted the opinion that hydrofluoric acid is a compound of a certain inflammable principle and oxygen, and applied to it the name of *fluoric acid*, previously introduced by Scheele. Fluor spar on this view is a fluate of lime, and when this salt is decomposed by oil of vitriol, the fluoric is merely displaced by the sulphuric acid, and the former passes off combined with the water of the latter. What I have described as anhydrous hydrofluoric acid is, according to this hypothesis, hydrated fluoric acid; and when acted upon by potassium, this metal is oxidized at the expense of the water, and potassa thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluate of potassa. The equivalent of fluoric acid, as inferred from the analysis of Berzelius, is 10.68; for 39.18 parts or one equivalent of fluor spar is supposed to contain 28.5 parts of lime (20.5 calcium and 8 oxygen), thus leaving 10.68 as the equivalent of the acid.

The theory according to which fluor spar is a compound of fluorine and calcium, originated as a suggestion with M. Ampère of Paris, and was afterwards supported experimentally by Davy. It was found that pure hydrofluoric acid evinces no sign of containing either oxygen or water. Charcoal may be intensely heated in the vapour of the acid without the production of carbonic acid. When hydrofluoric acid was neutralized with dry ammoniacal gas, a white salt resulted, from which no water could be separated; and on treating this salt with potassium, no evidence could be obtained of the presence of oxygen. On exposing the acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which from its combustibility was inferred to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate-coloured powder. Davy explained these phenomena by supposing that hydrofluoric acid was resolved into its elements; and that fluorine, at the moment of arriving at the positive side of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress, and examine the different products with that precision which is essential to the success of minute chemical inquiries, and which Davy has so frequently displayed on other occasions.

Though these researches led to no conclusive result, they afforded so strong a presumption in favour of the opinion of Ampère and Davy, that it was adopted by several other chemists. This view has received strong additional support from the experiments of M. Kuhlman. (Quarterly Journal of Science for July 1827, p. 205.) It was found by this chemist that fluor spar is not in the slightest degree decomposed by the action of anhydrous sulphuric acid, whether at common temperatures or at a red heat. The experiment was made both by transmitting the vapour of anhydrous sulphuric acid over fluor spar heated to redness in a tube of platinum, and by putting the mineral into the liquid acid. In neither case did decomposition ensue; but when the former experiment was repeated with the difference of employing concentrated hydrous instead of anhydrous sulphuric acid, evolution of hydrofluoric acid was produced. M. Kuhlman also transmitted dry hydrochloric acid gas over fluor spar at a red heat, when hydrofluoric acid was disengaged, without any evolution of hydrogen, and chloride of calcium remained. I am aware of no satisfactory explanation of these facts, except by regarding fluor spar as a compound of fluorine and calcium, and hydrofluoric acid as a compound of fluorine and hydrogen. I shall accordingly adopt this view in the subsequent pages, and never employ the term fluoric acid, except when explaining phenomena according to the theory of Gay-Lussac.

Fluoboric Acid.—The chief difficulty in determining the nature of hydrofluoric acid arises from the water of the sulphuric acid which is employed in its preparation. To avoid this source of uncertainty, Gay-Lussac and Thenard made a mixture of vitrified boracic acid and fluor spar, and exposed it in a leaden retort to heat, under the expectation that as no water was present anhydrous fluoric acid would be obtained. In this, however, they were disappointed; but a new gas came over, to which they applied the term of *fluoboric acid gas.* A similar train of reasoning led Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Another process, given by Dr. Davy, is to mix 1 part of vitrified boracic acid and 2 of fluor spar with 12 parts of strong sulphuric acid, and heating the mixture gently in a glass flask; (Phil. Trans.

1812;) but the gas thus developed contains a considerable quantity of fluosilicic acid. Fluoboric acid gas may also be formed by heating a strong solution of hydrofluoric and boracic acids in a metallic retort.

In the decomposition of fluor spar by vitrified boracic acid, the former and part of the latter undergo an interchange of elements. The fluorine uniting with boron gives rise to fluoboric acid gas; and by the union of calcium and oxygen, lime is generated, which combines with boracic acid, and is left in the retort as borate of lime. Fluoboric acid gas, therefore, is composed of boron and fluorine. Those who adopt the theory of Gay-Lussac give a different explanation, and regard this gas as a compound of fluoric and boracic acids. The lime of fluor spar is supposed to unite with one portion of boracic acid, and fluoric acid at the moment of separation with another, yielding borate of lime and fluoboric acid gas.

Fluoboric acid gas is colourless, has a penetrating pungent odour, and extinguishes flame on the instant. Its specific gravity, according to Dr. Thomson, is 2.3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluoborates*. It has a singularly great affinity for water. When mixed with air or any gas which contains watery vapour, a dense white cloud, a combination of water and fluoboric acid, appears, thus affording an extremely delicate test of the presence of moisture in gases. Water acts powerfully on this gas, absorbing, according to Dr. Davy, 700 times its volume, during which the water increases in temperature and volume. The solution is limpid, fuming, and very caustic. On the application of heat, part of the gas is disengaged; but afterwards the whole solution is distilled.

Gay-Lussac and Thenard, and Dr. Davy were of opinion that fluoboric acid gas is dissolved in water without decomposition; but Berzelius denies the accuracy of their observation. On transmitting the gas into water until the liquid acquires a sharply sour taste, but is far from being saturated, a white powder begins to subside; and, on cooling, a considerable quantity of boracic acid is deposited in crystals. It appears that in a certain state of dilution, part of the fluoboric acid and water mutually decompose each other, with formation of boracic and hydrofluoric acids. The latter unites, according to Berzelius, with undecomposed fluoboric acid, forming what he has called *boro-hydrofluoric acid.* On concentrating the liquid by evaporation, the boracic and hydrofluoric acids decompose each other, and the original compound is re-produced.

Fluoboric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sulphuric acid into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluoboric acid gas, the metal takes fire, and a chocolate-coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of boron and fluoride of potassium, from which the latter is dissolved by water, and the boron is left in a solid state.

The composition of fluoboric acid gas has not hitherto been determined by direct experiment. Dr. Davy ascertained that it unites with an equal measure of ammoniacal gas, forming a solid salt; and that it also combines with twice and three times its volume of ammonia, yielding liquid compounds. In the former salt the relative weights of the constituent gases are in the ratio of their specific gravities; and if the compound consists of one equivalent of each, it will be constituted of,

Fluoboric acid gas	-	2.3622	.-	68.69 one eq.
Ammoniacal gas	-	0.5897	-	17.15 one eq.

so that the equivalent of the acid may be assumed in round numbers to be 68. Now supposing this acid to be formed of three equivalents of fluorine and one of boron, its equivalent will be 66.94, a number which approximates to the preceding. This view is consistent with the composition of boracic acid as given at page 205, and with the conversion of fluoboric acid by water into hydrofluoric and boracic acids.

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

SECTION I.

HYDROGEN AND NITROGEN.—AMMONIACAL GAS.

The aqueous solution of ammonia, under the name of *spirit of hartshorn*, has been long known to chemists; but its existence as a gas was first noticed by Priestley, who described it in his works under the title of *alkaline air*. It is often called the *volatile alkali;* but the terms ammonia and ammoniacal gas are now usually employed.

The most convenient method of preparing ammoniacal gas for the purposes of experiment is by applying a gentle heat to the concentrated solution of ammonia, contained in a glass vessel. It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form, but when diluted with air, it may be taken into the lungs with safety. Burning bodies are extinguished by it, nor is the gas inflamed by their approach. Ammonia, however, is inflammable in a low degree; for when a lighted candle is immersed in it, the flame is somewhat enlarged, and tinged of a pale yellow colour at the moment of being extinguished; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark; water being formed, and nitrogen set free. A little nitric acid is generated at the same time, except when a smaller quantity of oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Dr. Henry, Philos. Trans. 1809.)

Ammoniacal gas at the temperature of 50° and under a pressure equal to 6.5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of —70°; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

Ammonia has all the properties of an alkali in a very marked manner. Thus it has an acrid taste, and gives a brown stain to turmeric paper; though the yellow colour soon reappears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts suffer decomposition by being heated with the fixed alkalies or alkaline earths, such as potassa or lime, the union of which with the acid of the salt causes the separation of its ammonia. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed, a character which manifestly arises from the volatile nature of the alkali. If combined with a volatile acid, such as the hydrochloric, the compound itself sublimes unchanged by heat; but when united with an acid, which is fixed at a low red heat, such as the phosphoric, the ammonia alone is expelled.

Hydrogen and nitrogen gases do not unite directly, and, therefore, chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting ammonia through porcelain tubes heated to redness. A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of 400 measures, 300 of which are hydrogen, and 100 nitrogen. Dr. Henry has made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (Annals of Philosophy, xxiv. 346.)

	Grains.
Now since 150 cubic inches of hydrogen weigh . .	3.2050
and 50 of nitrogen	15.0825
100 cubic inches of ammonia must weigh	18.2875

and it is composed by weight of

Hydrogen	3.2050	3	or three equivalents.
Nitrogen	15.0825	14.15	or one equivalent.

Its equivalent, therefore, is 17.15.

The specific gravity of ammonia, according to this calculation, is 0.5897, a number which agrees closely with those ascertained directly by Sir H. Davy and Dr. Thomson.

Ammoniacal gas has a powerful affinity for water, and for this reason must always be collected over mercury. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Davy, in his Elements, stated that water at 50°, and when the barometer stands at 29.8 inches, absorbs 670 times its volume of ammonia; and that the solution has a specific gravity of 0.875. According to Dr. Thomson, water at the common temperature and pressure takes up 780 times its bulk. By strong compression, water absorbs the gas in still greater quantity. Heat is evolved during its absorption; and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia, commonly though incorrectly termed *liquid ammonia*, is made by transmitting a current of the gas, as long as it continues to be absorbed, into distilled water, which is kept cool by means of ice or moist cloths. The gas may be prepared from any salt of ammonia by the action of any pure alkali or alkaline earth; but hydrochlorate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of hydrochlorate of ammonia and well-burned quicklime, considerable excess of lime being taken, in order to decompose the hydrochlorate more expeditiously and completely. The lime is slaked by the addition of water; and as soon as it has fallen into powder, it should be placed in an earthen pan and be covered till it is quite cold, in order to protect it from the carbonic acid of the air. It is then mixed in a mortar with the hydrochlorate of ammonia, previously reduced to a fine powder; and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually increased as long as a free evolution of gas continues. The ammonia should be conducted by means of a safety tube of Welter into a quantity of distilled water equal to the weight of the salt employed. The residue consists of chloride of calcium, and lime.

The concentrated solution of ammonia, as thus prepared, is a clear colourless liquid, of specific gravity 0.936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility, it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Sir H. Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different densities, at 59° F. and when the barometer stands at 30 inches. The specific gravity of water is supposed to be 10,000:

Table of the Quantity of real Ammonia in Solutions of different Densities.

100 parts of sp. gravity.		Of real Ammonia.	100 parts of sp. gravity.		Of real Ammonia.
8750	contain	32.5	9435	contain	14.53
8875		29.25	9476		13.46
9000		26.00	9513		12.40
9054		25.37	9545		11.56
9166		22.07	9573		10.82
9255		19.54	9597		10.17
9326		17.52	9619		9.60
9385		15.88	9692		9.50

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on yellow turmeric paper, and by its forming dense white fumes—hydrochlorate of ammonia—when a glass rod moistened with hydrochloric acid is brought near it.

SECTION II.

COMPOUNDS OF HYDROGEN AND CARBON.

Chemists have for several years been acquainted with two distinct compounds of carbon and hydrogen, viz. carburetted hydrogen and olefiant gases; but late researches have enriched the science with several other compounds of a similar nature, to which much interest is attached. They are remarkable for their number; for supplying some instructive instances of isomerism; for their tendency to unite with and even neutralize powerful acids, without, in their uncombined state, manifesting any ordinary signs of alkalinity; and some of them appear to act an important part in the formation of the ethers, camphor, and some other inflammable substances. The following tabular view represents the composition of those which have as yet been studied.

	Hydrogen.	Carbon.	Equiv.	Formulæ.
Light carburetted hydrogen	2 2 eq. +	6.12 1 eq. =	8.12	2H + C or H^2C.
Olefiant gas	2 2 eq. +	12.24 2 eq. =	14.24	2H + 2C or H^2C^2
Etherine	4 4 eq. +	24.48 4 eq. =	28.48	4H + 4C or H^4C^4.
Bicarburet of hydrogen	3 3 eq. +	36.72 6 eq. =	39.72	3H + 6C or H^3C^6.
Paraffine Eupione	Same ratio of elements as in etherine, but equivalent is unknown.			
Naphtha	5 5 eq. +	36.72 6 eq. =	41.72	5H + 6C or H^5C^6.
Naphthaline	4 4 eq. +	61.2 10 eq. =	65.2	4H + 10C or H^4C^{10}.
Paranaphthaline	6 6 eq. +	91.8 15 eq. =	97.8	6H + 15C or H^6C^{15}.
Idrialine	Ratio of carbon to hydrogen as 3 to 1, but equivalent unknown.			
Camphene Citrene	8 8 eq. +	61.2 10 eq. =	69.2	8H + 10C or H^8C^{10}

Light Carburetted Hydrogen.—This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, and *hydrocarburet*. Agreeably to the principles of chemical nomenclature, taking carbon as the electro-negative element, it is a *dicarburet of hydrogen;* but it is generally termed *light carburetted hydrogen.* It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime-water or a solution of pure potassa, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it. Light carburetted hydrogen is tasteless and nearly inodorous, and it does not change the colour of litmus or turmeric paper. Water, according to Dr. Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is unable to support the respiration of animals. It is highly inflammable; and when a jet of it is set on fire, it burns with a yellow flame, and with a much stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Dalton first ascertained the real nature of light carburetted hydrogen, and it has since been particularly examined by Thomson, Davy, and Henry. When 100 measures are detonated with rather more than twice their volume of oxygen gas, the whole of the inflammable gas and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. Now 100 measures of carbonic acid gas contain (page 187) 100 of carbon vapour and 100 of oxygen gas, just half the oxygen which had been employed; and the remaining oxygen requires 200 measures of hydrogen to form water. Hence as, at 60° F. and 30 inches Bar.,

			Grains.
100	cubic inches of	carbon vapour weigh . .	13.0714
200	do.	hydrogen gas	4.2734
100	do.	light carburetted hydrogen must weigh	17.3448

These weights are obviously in the ratio of 2 to 6.12 as already assigned; and the density of such a gas ought to be 0.5593, which is nearly the quantity found experimentally by Thomson and Henry.

Light carburetted hydrogen is not decomposed by electricity, nor by being passed through red-hot tubes, unless the temperature is very intense, in which case some of the gas does suffer decomposition, each volume yielding two volumes of pure hydrogen gas and a deposite of charcoal.

Chlorine and light carburetted hydrogen gas do not act on each other at common temperatures, when quite dry, even if exposed to the direct solar rays. If moist, and the mixture is kept in a dark place, still no action ensues; but if light be admitted, particularly sunshine, decomposition follows. The nature of the products depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and hydrochloric acid gases will be produced: two volumes of chlorine combined with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen, forming hydrochloric acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed. (Dr. Henry.) If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, hydrochloric acid is formed, and charcoal deposited.

It was first ascertained by Henry (Nicholson's Journal, vol. xix.), and his conclusions have been fully confirmed by the subsequent researches of Davy, that the *fire-damp* of coal mines consists almost solely of light carburetted hydrogen. This gas often issues in large quantity from between beds of coal, and by collecting in mines owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches, sets fire to the whole mass, and an explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety-lamp. For this invention we are indebted to Davy, who established the principles of its construction by a train of elaborate experiment and close reasoning, which may be regarded as one of the happiest efforts of his genius. (Essay on Flame.)

Davy commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with 3 or 4 times its volume of air, it does not explode at all. It detonates feebly when mixed with 5 or 6 times its bulk of air, and powerfully when 1 to 7 or 8 is the proportion. With 14 times its volume, it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature required for causing an explosion was next ascertained. It was found that the strongest explosive mixture may come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame cannot pass through a narrow tube. This led to the discovery, that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus a piece of fine wire gauze, which may be regarded as an assemblage of short narrow tubes, is quite impermeable to flame: and consequently if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an explosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire-damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gauze, and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdraw; for though the flame should not be able to communicate with the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Davy has shown that the temperature necessary for producing this effect is far higher than the white heat of solid bodies. Now when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much heat that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only;—the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of heat, it loses heat with great rapidity. Its temperature, therefore, though it may be heated to whiteness, is always so far below that of flame, as to exert a cooling influence over the burning gas, and reduce its heat below the point at which it is incandescent.

These principles suggest the conditions under which Davy's lamp would cease to be safe. If a lamp with its gauze red-hot be exposed to a *current* of explosive mixture, the flame may possibly pass so rapidly as not to be cooled below the point of ignition, and in that case an accident might occur with a lamp which would be quite safe in a calm atmosphere. It has been lately shown by Messrs. Upton and Roberts, lamp manufacturers of this city, that flame in this way may be made to pass through the safety-lamp as commonly constructed; and I am satisfied, from having witnessed some of their experiments, that the observation is correct. This then may account for accidents in coal mines where the safety-lamp is constantly employed. An obvious mode of avoiding such an evil is to diminish the apertures of the gauze; but this remedy is nearly impracticable from the obstacle which very fine gauze causes to the diffusion of light. A better method is to surround the common safety-lamp with a glass cylinder, allowing air to enter solely at the bottom of the lamp through wire gauze of extreme fineness, placed horizontally, and to escape at top by a similar contrivance. Upton and Roberts have constructed a lamp of this kind, through which I have in vain tried to cause the communication of flame, and which appears to me perfectly secure: in case an accident should break the glass, the lamp would be reduced to a safety-lamp of the common construction. Davy's lamp thus modified gives a much better light than without the glass, just as all lamps burn better with a shade than without one.

Olefiant Gas.—This gas was discovered in 1796 by some associated Dutch chemists, who gave it the name of *olefiant gas*, from its property of forming an oil-like liquid with chlorine. It is sometimes, but very improperly, called bicarburetted or percarburetted hydrogen. The ratio of its elements being as one to one suggests the term carburet of hydrogen; but this does not indicate that two equivalents of carbon are combined with two eq. of hydrogen to form one eq. of the gas. Perhaps the expression $\frac{2}{2}$ carburet of hydrogen will adequately express this, a principle of nomenclature already adopted by some of the German chemists.

Olefiant gas is prepared by mixing in a capacious retort six measures of strong alcohol with twelve of concentrated sulphuric acid, and heating the mixture, as soon as it is made, by means of an Argand lamp. The acid soon acts upon the alcohol, effervescence ensues, and olefiant gas passes over. The chemical changes which take place are of a complicated nature, and the products numerous. At the commencement of the process, the olefiant gas is mixed only with a little ether; but in a short time the solution becomes dark, the formation of ether declines, and the odour of sulphurous acid begins to be perceptible: towards the close of the operation, though olefiant gas is still the chief product, sulphurous acid is freely disengaged, some carbonic acid is formed, and charcoal in large quantity deposited. The olefiant gas may be collected either over water or mercury. The greater part of the ether condenses spontaneously, and the sulphurous and carbonic acids may be separated by washing the gas with lime-water, or a solution of pure potassa.

The olefiant gas in this process is derived solely from the alcohol; and its production is owing to the strong affinity of sulphuric acid for water. Alcohol is composed of carbon, hydrogen, and oxygen; and from the proportion of its elements it is inferred to be a compound of 14·24 parts or one equivalent of olefiant gas, united with 9 parts or one equivalent of water. It is only necessary, therefore, in order to obtain olefiant gas, to deprive alcohol of the water which is essential to its constitution; and this is effected by sulphuric acid. The formation of ether, which occurs at the same time, will be explained hereafter. The other phenomena are altogether extraneous. They almost always ensue when substances derived from the animal and vegetable kingdoms are subjected to the action of sulphuric a sweet taste and aromatic odour. It sinks rapidly in strong sulphuric acid. It is fused by heat, and then sublimed without change, condensing into crystals, which are either tabular or prismatic. On exposure to strong heat, it is decomposed, and iodine escapes. It burns, if held in the flame of a spirit-lamp, with evolution of iodine and some hydriodic acid. It is insoluble both in water and acid or alkaline solutions. Alcohol and ether dissolve it, and on evaporating the solution it crystallizes.

Iodide of hydrocarbon is composed, according to the analysis of Mr. Faraday, of 126.3 parts or one equivalent of iodine, and 14.24 parts, or one equivalent of olefiant gas. (Quarterly Journal of Science, xiii.)

Bromide of Hydrocarbon.—This compound was formed by Serullas, by adding one part of the iodide of hydrocarbon to two parts of bromine contained in a glass tube. Instantaneous reaction ensues, attended with disengagement of heat and a hissing noise, and two compounds, the bromide of iodine and a liquid bromide of hydrocarbon, are generated. By means of water the former is dissolved; while the latter, coloured by bromine, collects at the bottom of the liquid. The decoloration is then effected by means of caustic potassa. In order that the process should succeed, the iodide of hydrocarbon must not be in excess.

Bromide of hydrocarbon, after being washed with a solution of potassa, is colourless, heavier than water, very volatile, of a penetrating ethereal odour, and of an exceedingly sweet taste, which it communicates to water in which it is placed, in consequence of being slightly soluble in that liquid. It becomes solid at a temperature between 21° and 23° F. This compound is identical with that which M. Balard formed by letting a drop of bromine fall into a flask full of olefiant gas. (An. de Ch. et de Physique, xxxiv.)

Etherine.—The substance to which this name is now applied was first obtained and examined by Mr. Faraday. (An. of Phil. xxvii. 44.) In the process of compressing oil gas in strong copper globes for the supply of portable gas, the gas is subjected to a pressure equal to 30 atmospheres, and a volatile liquid collects, derived from inflammable vapours which were diffused through the gas. This liquid, when recently collected, boils at 60°. On simply heating it by the hand, and conducting the vapour through tubes cooled to 0° by a freezing mixture, the etherine is obtained in the form of a highly volatile liquid, which boils by slight elevation of temperature, and before the thermometer rises to 32° is wholly reconverted into vapour. It derives its name from being considered as an essential constituent of the ethers.

The vapour of etherine is highly combustible, and burns with a brilliant flame, yielding carbonic acid and water. On being cooled to 0° it is again condensed into a liquid, the density of which at 54° (being kept liquid by the pressure of its own vapour in a tube hermetically sealed) is 0.627; so that among solids and liquids it is the lightest body known.

Etherine is sparingly dissolved by water; but alcohol takes it up in large quantity, and the solution effervesces by dilution with water. Alkalies and hydrochloric acid do not affect it. Sulphuric acid absorbs more than 100 times its volume of the vapour, yielding a dark-coloured solution, but without evolution of sulphurous acid.

From the analysis of the vapour of etherine, made by detonating it with oxygen gas, Faraday infers that each volume requires six of oxygen for complete combustion, and yields four volumes of carbonic acid. Hence, 100 cubic inches of the vapour contain 400 of the vapour of carbon, and 400 of hydrogen gas; and since

		Grains.
400	cubic inches of carbon vapour weigh -	52.2856
400	" hydrogen gas - - -	8.5468
100	" etherine vapour should weigh	60.8324

These weights are in the ratio 24.48 or four equivalents of carbon to 4 or four eq. of hydrogen, being the composition already given in the table. density of its vapour should be 1.9616, while Mr. Faradayfound it 1.91 by observation.

Bicarburet of Hydrogen.—This compound was obtained by Faraday the same oil gas liquid which yielded etherine. As soon as the more tile parts are dissipated, which happens before one-tenth is thrown ofl point of ebullition rises to 100°; and it gradually ascends to 250° befoı the liquid is volatilized, indicating the presence of two or more compo differing in volatility. It was remarked that the boiling point was ı constant between 176° and 190° than at any other temperature; and or lecting the liquid which came over at that part of the process, distilling peatedly, and employing a cold of 0°, he succeeded in obtaining a subst of invariable character, to which he applied the name of *bicarburet of hy gen*, expressive of the ratio of its elements though not of their quantity.

Bicarburet of hydrogen, at common temperatures, is a colourless trar rent liquid, which smells like oil gas, and has also a slight odour of alm Its specific gravity is nearly 0.85 at 60° F. At 32° it is congealed, forms dendritic crystals on the sides of the glass. At zero it is transpa brittle, and pulverulent, and is nearly as hard as loaf-sugar. When exp to the air at the ordinary temperature it evaporates, and boils at 186°. density of its vapour at 60°, and when the barometer stands at 29.98 inc is nearly 2.7760.

Bicarburet of hydrogen is very slightly soluble in water; but it diss freely in fixed and volatile oils, in ether, and in alcohol, and the alcol solution is precipitated by water. It is not acted on by alkalies. It is bustible, and burns with a bright flame and much smoke. When admi to oxygen gas, so much vapour rises as to make a powerfully detona mixture. Potassium heated in it does not lose its lustre. On passing vapour through a red-hot tube, it gradually deposites charcoal, and yi carburetted hydrogen gas. Chlorine, by the aid of sunshine, decompos with evolution of hydrochloric acid. Two triple compounds of chlor carbon, and hydrogen are formed at the same time, one of which is a c talline solid, the other a dense thick fluid.

Bicarburet of hydrogen was analyzed in two ways. In the first, its va was passed over oxide of copper heated to redness; and in the second, it detonated with oxygen gas. Carbonic acid and water were the sole ducts: and as the absence of oxygen is established by the inaction of p sium, it follows that the bicarburet consists of carbon and hydrogen Mr. Faraday infers from his analyses, that 100 measures of the inflamn vapour require 750 of oxygen for complete combustion; that 150 mea of oxygen unite with 300 hydrogen; and that the remaining 600 con with 600 of the vapour of carbon, forming 600 measures of carbonic gas. Hence, as

	Grains.
600 cubic inches of carbon vapour weigh -	78.4284
300 - - hydrogen gas - -	6.4101
100 - - bicarburet vapour should weigh	84.8385

The ratio of these weights is 36.72 or six eq. of carbon to 3 or thre hydrogen as already stated. The calculated density is 2.7357, which agrees with the experimental number.

Paraffine.—This substance was discovered about the same time Reichenbach in Moravia, and by Dr. Christison. The latter obtain distillation from the petroleum of Rangoon, and in 1831 read a notic before the Royal Society of Edinburgh under the name of *petroli* former procured it by distilling tar derived from the igneous decom of vegetable matter, especially of beech wood; and applied to it th under which it has become known, compounded of *parum affinis*, *lit* to denote the remarkable chemical indifference which is its characteristic feature. (An. de Ch. et de Ph. 1. 69.)

In distilling beech-tar, three liquids are obtained, the heaviest of which is unctuous and contains the paraffine. It is purified in part by repeated distillation, and then heated to 212° with half its weight of strong sulphuric acid, whereby its impurities are decomposed, and the paraffine collects on cooling as a cake on the surface: for its more complete separation the acid should be kept at 112° for some hours. The paraffine is then removed, washed with water, pressed within folds of blotting paper, in order to imbibe some adhering oil, and is then dissolved in boiling very strong alcohol, out of which it crystallizes in cooling.

Paraffine at common temperatures is a rather firm solid, of density 0.87, fatty in aspect, is tasteless and inodorous, and separates from its alcoholic solution in thin laminæ of a lustre and appearance very like cholesterine. At 111° it fuses into a colourless oily liquid, and rises in vapour, evaporating without change. It is inflammable like the fats, and burns with a pure white flame, yielding carbonic acid and water.

Paraffine resists the action of all the acids, the alkalies, and chlorine, and may be fused without change. Fusion with camphor, naphthaline, and pitch causes no action; but it unites with stearine, cetine, and wax, when fused with them. Its best solvents are spirit of turpentine and naphtha, which dissolve it even in the cold; and the fat oils take it up readily by the aid of heat.

According to an analysis by J. Gay-Lussac, its sole elements are carbon and hydrogen, in the same ratio as in olefiant gas; but as neither its equivalent nor the density of its vapour are known, its atomic constitution is undetermined.

Eupione.—This substance, discovered and described by Dr. Reichenbach at the same time as paraffine, derives its name from *ευ well*, and *πιων greasy*, being analogous to oils in greasiness to paper and inflammability, though a much more perfect liquid, being as limpid as alcohol. It has no taste, colour, or odour, retains its liquid form at —4°, has a density of 0.74, and boils at 339°, evaporating without change or residue. In water it is insoluble; but it dissolves in ether, spirit of turpentine, naphtha, almond oil, bisulphuret of carbon, and alcohol. The latter is its best solvent: 100 parts of eupione dissolve in 33 of absolute alcohol at 63°, and in every proportion with the aid of heat. When kindled it burns with a lively flame, without smoke, and carbonic acid and water are its sole products.

Eupione dissolves camphor, stearine, cetine, cholesterine, naphthaline, and paraffine, especially when heated. It also dissolves chlorine, bromine, and iodine; but they are expelled by heat, and leave the eupione unchanged. It is not altered by exposure to the air, nor is it attacked by potassium, by the strong acids, or by the pure alkalies.

Eupione is associated with paraffine in animal and vegetable tar, being most abundant in the former, as paraffine is in the latter. It is best prepared by distillation from the tar derived from bones or horn, and is purified by repeated distillation from strong sulphuric acid. After being washed with an alkaline solution to remove adhering acid, its only remaining impurity is paraffine, the greater part of which crystallizes under a cold of 0°. The separation may also be effected by means of alcohol, and by cautious distillation along with water, since eupione is more soluble in alcohol and more volatile than paraffine. (An. de Ch. et de Ph. i. 60.)

The composition of eupione has not been determined. Judging from its properties it must be a compound of carbon and hydrogen, and propably differs from paraffine only in containing a smaller proportion of carbon.

Naphtha.—This name, from the Greek *ναφθα*, is applied to a volatile limpid liquid, of a strong peculiar odour, and generally of a light yellow colour; but it may be rendered colourless by careful distillation. Its specific gravity, when highly rectified, is 0.753 at 61° F. It is very inflammable, and burns with a white flame mixed with much smoke. In a platinum vessel it begins to boil at 158° F., but the thermometer is not stationary until it reaches 192°: its vapour has a density of 2.833. (Saussure.) It retains its liquid form at 0°. It is insoluble in water, but unites in every proportion with absolute alcohol, sulphuric ether, petroleum, and oils. By exposure to the air, it slowly absorbs oxygen, and at the same time gives out a little carbonic acid. The oxygen found in some specimens of naphtha is probably derived from this source. (An. de Ch. et de Ph. xlix. 240.)

When spirit of turpentine is deprived of all absorbed oxygen by the action of potassium, and is then carefully distilled, it is found to possess the recognized properties of naphtha, and to consist solely of carbon and hydrogen in the ratio of six eq. to five, a result formerly obtained by Saussure, and lately confirmed by Dumas. (An. de Ch. et de Ph. l. 238.)

Hence, regarding 100 measures of naphtha vapour to contain 600 measures of carbon vapour and 500 of hydrogen gas, then as

		Grains.
600	cubic inches of carbon vapour weigh . .	78.4284
500	. . hydrogen gas . .	10.6835
100	. . naphtha vapour should weigh .	89.1119

A vapour so constituted should have a density of 2.8735, which accords closely with that found by Saussure.

Naphtha occurs in some parts of Italy, and on the banks of the Caspian sea: the specimen examined by Saussure was from Amiano in the duchy of Parma. It is an ingredient of the dark bituminous liquid called petroleum, and may be obtained from it by distillation. Coal-tar yields by distillation a liquid very similar to mineral naphtha, and to all appearance identical with it; and the least volatile parts of the oil-gas liquor (page 251) appear to consist principally of naphtha.

Naphthaline.—This substance is one of the products of the destructive distillation of coal, and is contained along with naphtha in coal-tar. On distilling this matter by a very gentle heat, the naphtha passes over; and afterwards the less volatile naphthaline rises in vapour, and condenses as a white crystalline solid in the neck of the retort. It was first noticed in 1820 by Mr. Garden of Oxford-street, and afterwards described by Dr. Kid and Mr. Chamberlain. (Annals of Phil. xv. 74, xix. 143, and xxii. 103.)

Pure naphthaline is heavier than water, has a pungent aromatic taste, and a peculiar, faintly aromatic, odour, not unlike that of the narcissus. It is smooth and unctuous to the touch, is perfectly white, and has a silvery lustre. It fuses at 180°, and assumes a crystalline texture in cooling. It volatilizes slowly at common temperatures, and boils at 410° F., crystallizing as it condenses with remarkable facility in thin transparent laminæ.

Naphthaline is not very readily inflamed; but when set on fire it burns rapidly, and emits a large quantity of smoke. It is insoluble in cold, and very sparingly dissolved by hot water. Its proper solvents are alcohol and ether, especially the latter: its solubility is increased by heat, and it separates in a crystalline state by cooling or evaporation. It is also soluble in olive oil, spirit of turpentine, and naphtha. To test paper, it manifests neither acidity nor alkalinity. Alkalies do not act upon it. The acetic and oxalic acids dissolve it, forming pink-coloured solutions; hot hydrochloric acid dissolves it sparingly; and when boiled with nitric acid, the naphthaline is altered, and the acid decomposed. With sulphuric acid it enters into direct combination, forming a peculiar acid, the *sulphonaphthalic*, discovered by Mr. Faraday. (Phil. Trans. 1826.)

According to Dr. Oppermann, the elements of naphthaline are in the ratio of one eq. of hydrogen to three eq. of carbon, (Pog. Annalen, xxiii. 303,); but from the experiments on sulphonaphthalic acid by Faraday, whose results have been confirmed by Liebig and Wöhler, and from a late analysis of naphthaline by M. Laurent, it consists of carbon and hydrogen in the ratio of twenty eq. to eight eq., or of ten to four. On the hypothesis that 100 measures of naphthaline vapour contain 1000 measures of carbon vapour and 400 of hydrogen gas, then, since

		Grains.
1000	cubic inches of carbon vapour weigh . .	130.7140
400	. . hydrogen gas . .	8.5468
100	. . naphthaline vapour should weigh	139.2608

A vapour so constituted would have a density of 4.4906; whereas the density of naphthaline, as found experimentally by Dumas, is 4.528, thus confirming the foregoing hypothesis.

Sulphonaphthalic Acid.—This acid is made by melting naphthaline with half its weight of strong sulphuric acid, when a red-coloured liquid is formed, which becomes a crystalline solid in cooling. The mass is soluble in water, and the solution contains a mixture of sulphuric and sulphonaphthalic acids. On neutralizing with carbonate of baryta, the insoluble sulphate subsides, while the soluble sulphonaphthalate remains in solution; and on decomposing this salt by a quantity of sulphuric acid precisely sufficient for precipitating the baryta, pure sulphonaphthalic acid is obtained.

The aqueous solution of the acid, as thus formed, reddens litmus paper powerfully, and has a bitter acid taste. On concentrating by heat, the liquid at last acquires a brown tint, and if then taken from the fire becomes solid as it cools. If the concentration is effected by means of sulphuric acid in an exhausted receiver, the acid becomes a soft white solid, apparently dry, and at length hard and brittle. In this state it is chemically united with water, and deliquesces on exposure to the air; but in close vessels it undergoes no change during several months. Its taste, besides being bitter and sour, leaves a metallic flavour like that of cupreous salts. When heated in a tube at temperatures below 212°, it is fused without undergoing any other change, and crystallizes from centres in cooling. When more strongly heated, water is expelled and the acid appears to be anhydrous; but at the same time it acquires a red tint, and a faint taste of free sulphuric acid may be detected,—circumstances which indicate commencing decomposition. On raising the temperature still higher, the red colour first deepens, then passes into brown, and at length the acid is resolved into naphthaline, sulphurous acid, and charcoal; but in order thus to decompose all the acid, a red heat is requisite.

Sulphonaphthalic acid is readily soluble in water and alcohol, and is also dissolved by oil of turpentine and olive oil, in proportions dependent on the quantity of water which it contains. By the aid of heat it unites with naphthaline. It combines with alkaline bases, and forms neutral salts, which are called *sulphonaphthalates*. All these salts are soluble in water, and most of them in alcohol, and when exposed to heat in the open air, take fire, leaving sulphates or sulphurets according to circumstances.

From Mr. Faraday's analysis of the neutral sulphonaphthalate of baryta, it appears that 76.7 parts or one equivalent of baryta are combined with 210.6 parts, or what may be regarded as one equivalent, of sulphonaphthalic acid. These 210.6 parts were found to consist nearly of 80.2 parts or two eq. of sulphuric acid, 122.4 parts or twenty eq. of carbon, and 8 parts or eight eq. of hydrogen. It has not been demonstrated that sulphuric acid exists as such is the compound, nor is it known how its elements are arranged; but from some interesting facts noticed by Mr. Hennel and others, to be mentioned in the section on ether, it appears very probable that sulphonaphthalic acid is a direct compound of sulphuric acid and naphthaline.

Chloride of Naphthaline.—When a current of dry chlorine gas acts at common temperatures on naphthaline, heat is emitted, the mass fuses, hydrochloric acid gas escapes, and at length, after the full action of chlorine, a semi-fluid substance is left, which contains two chlorides, one solid and the other liquid. On agitating with successive portions of cold ether, the latter is dissolved, and the former obtained in a pure state.

The solid chloride is insoluble in water, and nearly so in hot alcohol, but may be dissolved, though not freely, by boiling ether, from which it separates on cooling in transparent rhomboidal laminæ of a vitreous lustre. At 320° it fuses, and at a higher temperature boils and is decomposed; but cautiously heated in a current of air, it may be distilled without change. The strong acids do not act upon it; nor is it decomposed by a solution of pure potassa except when heated with it.

The liquid chloride is obtained by evaporating its ethereal solution. It has the aspect of an oil, is of a light yellow colour, and sinks in water, in which it is insoluble. Alcohol readily dissolves it, and ether still more freely. It may be distilled without decomposition, and suffers little from the action of acids and alkalies.

The preceding facts were observed by M. Laurent. (An. de Ch. et de Ph. lii. 275.) From his analysis the solid chloride consists of 70.84 parts or two eq. of chlorine, united with a carburet of hydrogen composed of 61.2 parts or ten eq. of carbon, and 3 parts or three eq. of hydrogen; as expressed by the formula $H^3 C^{10} + Cl^2$. The liquid chloride was found to contain 35.42 parts or one eq. of chlorine, 61.2 or ten eq. of carbon, and 4 parts or four eq. of hydrogen, being the ingredients of chloride of naphthaline, of which the formula is $H^4 C^{10} + Cl$. Some doubt may, however, be entertained of its real composition, since the liquid chloride is apt to contain some of the solid compound in solution.

Paranaphthaline.—This substance is so called from *παρα near to*, because it is very closely allied to naphthaline both in chemical properties and composition, is associated with it in coal-tar, and obtained by the same process. Being less volatile than naphthaline it comes over in the after part of the distillation.

Paranaphthaline fuses at 356°, and boils at a heat beyond 572°, being partly decomposed at the same rate. It is insoluble in water, and nearly so in alcohol and ether. Its best solvent is spirit of turpentine. The density of its vapour is 6.741, and its elements are in the same ratio as in naphthaline; whence it is thought to consist of 1500 measures of carbon vapour and 600 of hydrogen gas condensed into 100 measures. A vapour so constituted should have a density of 6.7359.

These facts were observed by Dumas and Laurent. (An. de Ch. et de Ph. l. 187.) In a critique on their essay Reichenbach states that paranaphthaline was obtained some years ago by Vogel, and that it is a mixture of paraffine and naphthaline. (Pog. Annalen, xxviii. 484.)

Idrialine.—This substance was obtained by Dumas from a mineral from the quicksilver mines at Idria in Carniola, whence he applied to it the name of *idrialine.* In its properties it is very similar to paranaphthaline, but is less fusible and less volatile. In order to sublime it unchanged, it must be heated in a current of carbonic acid gas. It is insoluble in water, and very sparingly soluble in alcohol and ether; but boiling spirit of turpentine takes it up and deposites it again rapidly as it cools. Hot sulphuric acid dissolves it, and acquires at the same time a beautiful blue tint, like sulphate of indigo, an appearance which is characteristic of idrialine. Respecting its composition nothing farther is known than that it consists of carbon and hydrogen in the ratio of three eq. of the former to one eq. of the latter. (An. de Ch. et de Ph. l. 193.)

Camphene.—From late researches by Dumas, it appears that several of the volatile oils consist essentially of compounds of carbon and hydrogen, which are capable, like cyanogen, of uniting successively with other substances, without undergoing any change in their own constitution. The compound which he has principally examined is the basis of camphor, hence called *camphogen* or *camphene*, which appears to exist in turpentine. From a sample of turpentine believed to have been brought from Savoy or Switzerland, Dumas distilled off an essence or volatile oil, which he supposes to be camphene in a state of purity; it is, in fact, a very pure essence of turpentine, colourless, limpid, volatile, inflammable, and possessed of the characteristic odour of that liquid. Its boiling point is 312° F. From the density of its vapour and the ratio of its elements, Dumas infers that 100 measures of camphene vapour contain 1000 measures of carbon vapour and 800 of hydrogen gas; so that since

	Grains.
1000 cubic inches of carbon vapour weigh . .	130.7140
800 do. hydrogen gas	17.0936
100 cubic inches of camphene vapour should weigh	147.8076

The weights 130.7140 and 17.0936 are in the ratio of 61.2 parts or ten eq. of carbon, to 8 parts or eight eq. of hydrogen, as indicated by the formula $H^8 C^{10}$. The density of its vapour should be 10×0.4215 or $4.215 + 8 \times 0.0689$ or $0.5512 = 4.7662$, which agrees with observation.

Camphene unites with oxygen in two proportions, and gives rise to camphor and camphoric acid; and with hydrochloric acid it yields a perfectly neutral compound called *artificial camphor*. These compounds, which will be described hereafter, are thus constituted: (An. de Ch. et de Ph. l. 225.)

	Camphene.				Equiv.	Formulæ.
Camphor .	69.2	1 eq. +	Oxygen	8	1 eq. = 77.2	$H^8 C^{10} + O$
Camphoric acid	138.4	2 eq. +	ditto	40	5 eq. = 178.4	$2H^8 C^{10} + 5O$
Artificial camphor	69.2	1 eq. +	Hyd. ac.	36.42	1 eq. = 105.62	$H^8 C^{10} + HCl$.

Citrene.—This substance is so called from being the essential and almost sole ingredient of the volatile oil of lemons. Its elements are in exactly the same ratio as in camphene, but are one-half less condensed; so that it may be viewed as a compound of four eq. of hydrogen to five eq. of carbon, indicated by the formula $H^4 C^5$.

Coal and Oil Gas.—The nature of the inflammable gases derived from the destructive distillation of coal and oil was first ascertained by Dr. Henry,* who showed, in several elaborate and able essays, that these gaseous products do not differ essentially from each other, but consist of a few well-known compounds, mixed in different and very variable proportions. The chief constituents were found to be light carburetted hydrogen and olefiant gases; but besides these ingredients, they contain an inflammable vapour, free hydrogen, carbonic acid, carbonic oxide, and nitrogen gases. The discoveries of Mr. Faraday have elucidated the subject still further, by proving that there exists in oil gas, and by inference in coal gas also, the vapour of several definite compounds of carbon and hydrogen, the presence of which, for the purposes of illumination, is exceedingly important.

The illuminating power of the ingredients of coal and oil gas is very unequal. Thus the carbonic oxide and carbonic acid are positively hurtful; that is, the other gases would give more light without them. The nitrogen of course can be of no service. The hydrogen is actually prejudicial; because, though it evolves a large quantity of heat in burning, it emits an exceedingly feeble light. The carburets of hydrogen are the real illuminating agents, and the degree of light emitted by these is dependent on the quantity of carbon which they contain. Thus olefiant gas illuminates much more powerfully than light carburetted hydrogen; and for the same reason, the dense vapour of etherine emits a far greater quantity of light, for equal volumes, than olefiant gas.

From these facts, it is obvious that the comparative illuminating power of different kinds of coal and oil gas may be estimated, approximately at least, by determining the relative quantities of the denser carburets of hydrogen which enter into their composition. This may be done in three ways. 1. By their specific gravity. 2. By the relative quantities of oxygen required for their complete combustion. 3. By the relative quantity of gaseous matter condensible by chlorine in the dark; for chlorine, when light is excluded, condenses all the hydrocarburets, excepting light carburetted hydrogen. Of these methods, the last is, I conceive, the least exceptionable.*

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* Nicholson's Journal of 1805. Phil. Trans. 1808, and 1821.

The formation of coal and oil gas is a process of considerable delicacy. Coal gas is prepared by heating coal to redness in iron retorts. The quality of the gas, as made at different places, or at the same place at different times, is very variable; the specific gravity of some specimens having been found as low as 0.42, and that of others as high as 0.700. These differences arise in part from the nature of the coal, and partly from the mode in which the process is conducted. The regulation of the degree of heat is the chief circumstance in the mode of operating, by which the quality of the gas is affected. That its quality may be influenced from this cause is obvious from the fact, that all the dense hydrocarburets are resolved by a strong red heat either into charcoal and light carburetted hydrogen, or into charcoal and hydrogen gas. Consequently the gas made at a very high temperature, though its quantity may be comparatively great, has a low specific gravity, and illuminates feebly. It is, therefore, an object of importance that the temperature should not be greater than is required for decomposing the coal effectually, and that the retorts be so contrived as to prevent the gas from passing over a red-hot surface subsequently to its formation.

These remarks apply with still greater force to the manufacture of oil gas; because oil is capable of yielding a much larger quantity of the heavy hydrocarburets than coal. The quality of oil gas from the same material is liable to such great variation from the mode of manufacture, that the density of some specimens has been found as low as 0.464, and that of others as high as 1.110. The average specific gravity of oil gas is 0.900, and it should never be made higher. The interest of the manufacturer is to form as much olefiant gas as possible, with only a small proportion of the heavier hydrocarburets. If the latter predominate, the quantity of gas derived from a given weight of oil is greatly diminished; and a subsequent loss is experienced by the condensation of the inflammable vapours when the gas is compressed, or while it is circulating through the distributing tubes.

Coal gas, when first prepared, always contains hydrosulphuric acid, and for this reason must be purified before being distributed for burning. The process of purification consists in passing the gas under strong pressure through milk of lime, or causing it to descend through successive layers of dry hydrate of lime. The latter method has this advantage over the former, that while it deprives the gas completely of hydrosulphuric acid, there is no loss from absorption of olefiant gas or the heavy hydrocarburets, as ensues when milk of lime is employed. But coal gas, after being thus purified, still retains some compound of sulphur, most probably, as Mr. Brande conjectures, sulphuret of carbon, owing to the presence of which a minute quantity of sulphurous acid is generated during its combustion. Oil gas, on the contrary, needs no purification; and as it is free from all compounds of sulphur, it does not yield any sulphurous acid in burning, and is, therefore, better fitted for lighting dwelling-houses than coal gas.

With respect to the relative economy of the two gases, I may observe that the illuminating power of oil gas, of specific gravity 0.900, is about double that of coal gas of 0.600. In coal districts, however, oil gas is fully three times the price of coal gas, and, therefore, in such situations, the latter is considerably cheaper. (Essay above quoted.)

A successful attempt has been made by Mr. Daniell to procure a gas, similar to that from oil in being free from sulphur, but made with cheaper materials. The substance employed for this purpose is a solution of common resin in oil of turpentine. The combustible liquid is made to drop into red-hot retorts in the same manner as oil; and the oil of turpentine, which from its volatility is driven off in vapour, is collected, and again used as a menstruum. For this process Mr. Daniell has taken out a patent, and the gas so prepared is employed for filling portable lamps. The gas, when properly made, is said to be of a very superior quality, and nearly if not quite equal to oil gas. A patent has also been taken for the formation of gas from a volatile oil, prepared during the destructive distillation of resin, and a manufacture both of the oil and gas is established at Hammersmith, near London.

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* For a discussion of this and other questions relative to oil and coal gas, the reader may consult an essay by Dr. Christison and myself in the Edinburgh Philosophical Journal of 1825.

SECTION III.

COMPOUNDS OF HYDROGEN AND SULPHUR.

Sulphur unites with hydrogen in at least two proportions, and the resulting compounds are thus constituted:—

	Hydrogen.	Sulphur.	Equiv.	Formulæ.
Hydrosulphuric acid	1	1 eq. + 16.1	1 eq. = 17.1	$H+S$ or HS.
Persulphuret of hydrogen	1	1 eq. + 32.2	2 eq. = 33.2	$H+2S$ or HS^2.

Hydrosulphuric Acid.—This compound is also known under the name of sulphuretted hydrogen. The best method of preparing it, is by heating sesquisulphuret of antimony in a retort, or other convenient glass vessel, with four or five times its weight of strong hydrochloric acid; when, by an interchange of elements, sesquichloride of antimony and hydrosulphuric acid are generated, the latter of which escapes with effervescence. The elements concerned before and after the change, are

1 eq. sesquisulphuret of antimony and 3 eq. hydrochloric acid
$2Sb+3S$ $\qquad\qquad$ $3(H+Cl)$

which yield

3 eq. hydrosulphuric acid and 1 eq. sesquichloride of antimony.
$3(H+S)$ $\qquad\qquad$ $2Sb+3Cl$.

It may also be formed by the action of sulphuric acid diluted with 3 or 4 parts of water on protosulphuret of iron: this sulphuret and water interchange elements, hydrosulphuric acid and protoxide of iron are generated, and the latter unites with sulphuric acid, while the former in the state of gas is rapidly disengaged. Hydrochloric acid may be substituted for the sulphuric. A sulphuret of iron may be procured for the purpose, either by igniting common iron pyrites, by which means nearly half of its sulphur is expelled, or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one part of sulphur. The materials should be placed in a common earthen or cast-iron crucible, and be protected as much as possible from the air during the process. The sulphuret procured from iron filings and sulphur always contains some uncombined iron, and, therefore, the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is immaterial.

Hydrosulphuric acid is a colourless gas, which reddens moist litmus paper feebly, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50°, it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed. To animal life it is very injurious. According to Dupuytren and Thenard, the presence of 1-1500th of this gas is instantly fatal to a small bird; 1-1000th killed a middle-sized dog; and a horse died in an atmosphere which contained 1-250th of its volume.

Hydrosulphuric acid extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphurous acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark: if 100 measures of it are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain. (Dr. Thomson.) From the result of this experiment, the composition of hydrosulphuric acid gas may be inferred; for it is clear, from the composition of sulphurous acid, (page 193,) that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, hydrosulphuric acid contains its own volume of hydrogen gas, and 16.66 of the vapour of sulphur; and since

		Grains.
16.66	cubic inches of the vapour of sulphur weigh .	34.4012
100	cubic inches of hydrogen gas weigh . . .	2.1367
100	cubic inches of hydrosulph. acid gas must weigh	36.5379

The sp. gravity of a gas so constituted should be 1.1782, which agrees with observation; and its elements are in the ratio of 1 to 16.1 as already mentioned.

The accuracy of this view is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard, the weight of 100 cubic inches of hydrosulphuric acid gas is 36.33 grains. When sulphur is heated in hydrogen gas, hydrosulphuric acid is generated without any change of volume. On igniting platinum wires in it by means of the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains; and a similar effect is produced, though more slowly, by a succession of electric sparks. (Elements of Sir H. Davy, p. 282.) Gay-Lussac and Thenard found that on heating tin in hydrosulphuric acid gas, sulphuret of tin is formed; and when potassium is heated in it, vivid combustion ensues, with formation of sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it was derived. (Recherches Physico-Chimiques, vol. i.)

The salts of hydrosulphuric acid are called *hydrosulphates*, and sometimes *hydrosulphurets*. This acid, however, rarely unites directly with metallic oxides; but in most cases its hydrogen combines with the oxygen of the oxide, and its sulphur with the metal. All the hydrosulphates which do exist are decomposed by sulphuric or hydrochloric acid, and hydrosulphuric acid gas is disengaged with effervescence.

Recently boiled water absorbs its own volume of hydrosulphuric acid, becomes thereby feebly acid, and acquires the peculiar odour and taste of sulphurous springs. The gas is expelled without change by boiling the water.

The elements of hydrosulphuric acid may easily be separated from one another. A solution of the gas cannot be preserved in an open vessel, because its hydrogen unites with the oxygen of the atmosphere, and sulphur is deposited. When mixed with sulphurous acid, both compounds are decomposed, water is generated and sulphur set free. On pouring into a bottle of the gas a little fuming nitric acid, mutual decomposition ensues, a bluish-white flame frequently appears, sulphur and nitrous acid fumes come into view, and water is generated. Chlorine, iodine, and bromine decompose it, with separation of sulphur, and formation of hydrochloric, hydriodic, and hydrobromic acids. An atmosphere charged with hydrosulphuric acid gas may be purified by means of chlorine in the space of a few minutes.

Hydrosulphuric acid gas is readily distinguished from other gases by its odour, by tarnishing silver with which it forms a sulphuret, and by the character of the precipitate which it produces with solutions of arsenious acid, tartar emetic, and salts of lead.

The most delicate test of its presence, when diffused in the air, is moist carbonate of oxide of lead spread on white paper.

Persulphuret of Hydrogen.—Though Scheele discovered this compound, it was first specially described by Berthollet. (An. de Chimie, xxv.) When protosulphuret of potassium (or of any metal of the alkalies and alkaline earths) is mixed in solution with sulphuric acid, the oxygen of water unites with potassium and its hydrogen with sulphur, just as when protosulphuret of iron is employed, hydrosulphuric acid and sulphate of potassa being generated: the elements $K + S$ and $H + O$ mutually interchange, and yield $K + O$ and $H + S$. If the potassium be combined with two or more equivalents of sulphur as in the so called *liver of sulphur* made by fusing carbonate of potassa with half of its weight of sulphur, then one of two events will happen, the hydrogen of the decomposed water will either unite with one eq. of sulphur and form hydrosulphuric acid, the superfluous sulphur subsiding in the form of a gray hydrate, or with two eq. of sulphur, and give rise to persulphuret of hydrogen. Now the former of these changes always occurs when the acid is added to the persulphuret of potassium; and the latter takes place when a concentrated solution of that sulphuret is added by little and little to the acid, provided the acid is in considerable excess, and the mixture well stirred after each addition. The same phenomena ensue when hydrochloric instead of sulphuric acid is employed: but then there are two sources from which hydrogen may be supplied. It may be derived, as above, from decomposed water, hydrochlorate of potassa being generated; or hydrochloric acid itself may be decomposed, its hydrogen uniting with sulphur and its chlorine with potassium. On all such occasions I adopt the latter view, and will give reasons for doing so in the section introductory to the study of the metals.

Such are the principles to be attended to in preparing persulphuret of hydrogen. In practice it is conveniently made by boiling equal parts of recently slaked lime and flowers of sulpur with 5 or 6 parts of water for half an hour, when a deep orange-yellow solution is formed, which contains persulphuret of calcium. Let this liquid be filtered, and gradually added cold to an excess of hydrochloric acid diluted with about twice its weight of water, briskly stirring. A copious deposite of hydrated sulphur falls (the Sulphur Præcipitatum of the London Pharmacopœia), and persulphuret of hydrogen gradually subsides in the form of a yellowish semi-fluid matter like oil. The change which ensues in the formation of the yellow solution may be theoretically represented thus:—

2 eq. lime & 6 eq. sulphur yield 1 eq. hyposulph. acid & 2 eq. bisulphuret calcium.
$2(Ca+O)$ $6S$ $2S+2O$ $2(Ca+2S)$.

The hyposulphurous acid exists in solution united with lime, and is decomposed when hydrochloric acid is added, resolving itself into sulphurous acid and sulphur (page 197), a change not essentially connected with the production of persulphuret of hydrogen, but resulting from the mode of preparing the persulphuret of calcium. It is probable that the calcium is combined with more than two eq of sulphur, and that the deposited sulphur is derived from that source as well as from decomposed hyposulphurous acid.

From the facility with which this substance resolves itself into sulphur and hydrosulphuric acid, its history is imperfect: indeed we are indebted to a recent essay by Thenard for the principal facts which are known. (An. de Ch. et de Ph. xlviii. 79.) At common temperatures it is a viscid liquid of a yellow colour, with a density of about 1.769, and a consistence varying between that of a volatile and fixed oil. It has the peculiar odour and taste of hydrosulphuric acid, though in a less degree. Its elements are so feebly united, that in the cold it gradually resolves itself into sulphur and hydrosulphuric acid, and suffers the same change instantly by a heat considerably short of 212° F. Decomposition is also produced by the contact of most substances, especially of metals, metallic oxides, even the alkalies, and metallic sulphurets. Thus effervescence from the escape of hydrosulphuric acid gas is produced by peroxide of manganese, silica, the alkaline earths in powder, and solutions of potassa or soda; and the oxides of gold and silver are reduced by it with such energy, that they are rendered incandescent. It is remarkable that the substance which causes the decomposition, often undergoes no chemical change whatever. In these respects persulphuret of hydrogen bears a close analogy to peroxide of hydrogen, and Thenard has traced other points of resemblance. They are both, for instance, rendered more stable by the presence of acids; they both whiten the tongue and skin when applied to them, and they are both possessed of bleaching properties.

The composition of persulphuret of hydrogen has been variously stated. According to Dalton it is a bisulphuret, consisting of two equivalents of sulphur, and one of hydrogen; and this view of its composition is corroborated by Sir John Herschel's analysis of persulphuret of calcium. (Edin. Phil. Journal, i. 13.) But Thenard found its constituents to vary; whence it is probable that hydrogen is capable of uniting with sulphur in several proportions.

Persulphuret of hydrogen is sometimes regarded as an acid; and on this supposition it may be termed *hydropersulphuric acid*, and its salts *hydropersulphates*. This view is founded on the hypothesis, that the solutions formed by boiling lime or an alkali with sulphur contain hyposulphite and hydropersulphate of lime, the hydrogen in the one acid and oxygen in the other being attributed to decomposed water, and not hyposulphite of lime and persulphuret of calcium as I have supposed. The latter view is more consistent with the fact that persulphuret of hydrogen in its free state has no acidity, and exhibits no tendency to unite with alkalies.

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SECTION IV.

HYDROGEN AND SELENIUM.—HYDROSELENIC ACID.

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen*, or *hydroselenic acid*. This gas is disengaged by the action of dilute sulphuric or hydrochloric acid on a protoseleniuret of any of the more oxidable metals, such as potassium, calcium, manganese, or iron, the explanation being the same as in the formation of hydrosulphuric acid from protosulphuret of iron.

Hydroselenic acid gas is colourless. Its odour is at first similar to that of hydrosulphuric acid; but it afterwards irritates the lining membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The acid is soon decomposed by exposure to the atmosphere; for the oxygen of the air unites with the hydrogen of the hydroselenic acid, and selenium, in the form of a red powder, subsides. It is decomposed by nitric acid and chlorine in the same manner as hydrosulphuric acid; and like that gas it decomposes many metallic salts, the hydrogen of the acid combining with the oxygen of the oxide, while an insoluble seleniuret of the metal is generated.

According to the analysis of Berzelius, hydroselenic acid consists of 39.6 parts or one eq. of selenium, and 1 part or one eq. of hydrogen; so that its equivalent is 40.6, and its formula $H + Se$ or HSe.

SECTION V.

COMPOUNDS OF HYDROGEN AND PHOSPHORUS.

Most chemists admit the existence of two compounds of phosphorus and hydrogen, the phosphuretted and perphosphuretted hydrogen, the constitution and properties of which have of late been closely studied by Dumas, Buff, and Rose. (An. de Ch. et de Ph. xxxi. 113, xli. 220, and li. 5.) Much uncertainty exists respecting the composition of the latter; but there is strong concurrent testimony to prove that phosphuretted hydrogen consists of 31.4 parts or two equivalents of phosphorus, and 3 parts or three eq. of hydrogen. Its equivalent should, therefore, be 34.4, and its formula $3H + 2P$, or H^3P^2.

Phosphuretted Hydrogen.—This gas, which was discovered in 1812 by Sir H. Davy, is colourless, and has a disagreeable odour, somewhat like that of garlic. Water absorbs about one-eighth of its volume. It does not take fire spontaneously, as perphosphuretted hydrogen does, when mixed with air or oxygen at common temperatures; but the mixture detonates with the electric spark, or at a temperature of 300° F. Even diminished pressure causes an explosion; an effect which, in operating with a mercurial trough, is produced simply by raising the tube, so that the level of the mercury within may be a few inches higher than at the outside. Admitted into a vessel of chlorine it inflames instantly, and emits a white light, a property which it possesses in common with perphosphuretted hydrogen. Its specific gravity was found by Dumas to be 1.214, and by Rose 1.154.

Davy prepared this gas by heating hydrated phosphorous acid in a retort (page 201); and it is also evolved from hydrous hypophosphorous acid by similar treatment. It is also formed, according to Dumas, by the action of strong hydrochloric acid on phosphuret of calcium; and likewise by the spontaneous decomposition of perphosphuretted hydrogen.

Phosphuretted hydrogen frequently contains free hydrogen gas, especially when a strong heat is used in its preparation, an impurity which may be detected by agitation with a cold saturated solution of sulphate of oxide of copper. This substance has the property of absorbing both of the compounds of phosphorus and hydrogen entirely, with production of phosphuret of copper, while the free hydrogen gas remains.

Dumas ascertained the composition of phosphuretted hydrogen by introducing into a tube containing the gas a fragment of bichloride of mercury, applying heat so as to convert it into vapour. Mutual decomposition instantly took place: phosphuret of mercury and hydrochloric acid were generated; and 100 measures of gas, thus decomposed, yielded 300 measures of hydrochloric acid gas, corresponding to 150 of hydrogen. The quantity of hydrogen contained in any given volume of phosphuretted hydrogen is thus found; and the weight of the former deducted from that of the latter gives the quantity of combined phosphorus. This inference is conformable to the quantity of oxygen required for the combustion of phosphuretted hydrogen. Dr. Thomson affirms that when this gas is detonated with 1.5 of its volume of oxygen gas, the only products are water and phosphorous acid; but that when the oxygen is in considerable excess, two volumes disappear for one of the compound, and water and phosphoric acid are generated. Now the hydrogen contained in one volume of phosphuretted hydrogen is equal to 1.5, and it unites with 0.75 of oxygen. Hence if 0.75, or $\frac{3}{4}$, be deducted from 1.5 and from 2. the remainders, $\frac{3}{4}$ and $\frac{5}{4}$, represent the relative quantity of oxygen which is required to convert the same weight of phosphorus into phosphorous and phosphoric acid. These numbers are obviously in the ratio of 3 to 5, as already stated on the authority of Berzelius. (Page

200.) The elements of the calculation have been confirmed both by Dumas and Buff.

Agreeably to these views, and to the combining volume of phosphorus (page 146), 100 measures of phosphuretted hydrogen gas contain 150 of hydrogen gas and 25 of the vapour of phosphorus; and hence, as

			Grains.
150	cubic inches of	hydrogen gas weigh	3.2050
25	do.	phosphorus vapour weigh . . .	33.5461
100	do.	phosphuretted hydrogen gas should weigh	36.7511

The calculated density of a gas so constituted should be 1.1850, which is nearly a mean of the observations of Dumas and Rose.

If the equivalent of phosphorus were 31.4 instead of 15.7, as is very far from improbable, then the combining volume of phosphorus vapour would be 50 instead of 25 (page 146); and phosphuretted hydrogen would consist of 50 measures of phosphorus vapour and 150 of hydrogen gas condensed into 100 measures, thus agreeing in composition with ammoniacal gas.*

Phosphuretted hydrogen has neither an acid nor alkaline reaction; but in its chemical relations it inclines to alkalinity. Thus it unites with hydrobromic and hydriodic acids, forming definite compounds which crystallize in cubes; and Rose finds that it unites with metallic chlorides, forming compounds analogous to those which ammonia forms with metallic chlorides.

Perphosphuretted Hydrogen.—The gas to which this name is applied, was discovered in the year 1783 by M. Gengembre, and has since been particularly examined by Dalton, Thomson, Dumas, and Rose. It may be prepared in several ways. The first method is by heating phosphorus in a strong solution of pure potassa; the second by heating a mixture made of small pieces of phosphorus and recently slaked lime, to which a quantity of water is added sufficient to give it the consistence of thick paste; and the third by the action of dilute hydrochloric acid, aided by moderate heat, on phosphuret of calcium. In these processes, three compounds of phosphorus are generated;—phosphoric acid, hypophosphorous acid, and perphosphuretted hydrogen—all of which are produced by decomposition of water, and the union of its elements with separate portions of phosphorus. The last method appears to yield the purest gas.

The gas obtained by either of these processes is said by Dalton to be generally, and by Dumas to be always, mixed with variable proportions of hydrogen; but Rose denies that free hydrogen gas is evolved, except when the heat is so great as to decompose the hypophosphite, a temperature which is never attained so long as the materials are moist. It has a peculiar odour, resembling that of garlic, and a bitter taste. Its density is estimated at 0.9027 by Thomson, at 1.1 nearly by Dalton, at 1.761 by Dumas, and 1.1935 by Rose. It has no action on test paper. Recently boiled water absorbs $\frac{1}{40}$th of its bulk of this gas, most of which is expelled by boiling or agitation with other gases. Like phosphuretted hydrogen it is freely absorbed by a solution of chloride of lime or sulphate of oxide of copper, by which means its purity may be ascertained, and the presence of hydrogen detected; and like that compound it sometimes decomposes metallic salts in the same manner as hydrosulphuric acid, giving rise to the formation of water and a phosphuret of the metal. But if the metal have a feeble affinity for oxygen, both the phosphurets of hydrogen throw it down in the metallic state, and water and phosphoric acid are generated. This is the case, according to Rose, with solutions of gold and silver.

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* This statement is inaccurate. On the supposition made by Dr. Turner, phosphuretted hydrogen would consist of 50 measures of phosphorus vapour and 300 of hydrogen gas, condensed into 200 measures. Consequently, it would not agree in composition with ammoniacal gas.—*Ed.*

Perphosphuretted hydrogen does not support combustion nor respiration. In most of its properties it resembles phosphuretted hydrogen; but from that gas as well as from other gases, it is distinguished by being spontaneously inflammable when mixed with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may arise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke, which enlarges as it ascends, and retains its shape, if the air is tranquil, until it disappears. The wreath is formed by the products of the combustion—metaphosphoric acid and water. If received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. It is remarkable that whatever may be the excess of oxygen, traces of phosphorus always escape combustion; but that if the gas be previously mixed with three times its volume of carbonic acid, and be then mixed with oxygen, the combustion is perfect. Dalton observed that it may be mixed with pure oxygen in a tube three-tenths of an inch in diameter without taking fire; but that the mixture detonates when an electric spark is transmitted through it.

In consequence of the combustibility of perphosphuretted hydrogen, it would be hazardous to mix it in any quantity with air or oxygen gas in close vessels. For the same reason care is necessary in the formation of this gas, lest, in mixing with the air of the apparatus, an explosion ensue, and the vessel burst. The risk of such an accident is avoided, when phosphuret of calcium is used, by filling the flask or retort entirely with dilute acid; and in either of the other processes, by causing the phosphuretted hydrogen to be formed slowly at first, in order that the oxygen gas within the apparatus may be gradually consumed. A very simple method of averting all danger has been mentioned by Mr. Graham. It consists in moistening the interior of the retort with one or two drops of ether, the vapour of which, when mixed with atmospheric air even in small proportion, effectually prevents the combustion of perphosphuretted hydrogen.

Great uncertainty exists respecting the composition of this gas. It seems pretty certain, from the experiments of Dumas and Rose, that 100 measures of it contain 150 of hydrogen; but the quantity of phosphorus combined with that hydrogen is a point by no means agreed on. The weight of phosphorus united with 1 part of hydrogen is estimated by Thomson at 12, by Rose at 10.52, and at 15.9 by Dumas. Such discordant estimates are only referable to the changeable nature of the gas itself. Perphosphuretted hydrogen, as first prepared, not only often contains variable quantities of the vapour of phosphorus, of free hydrogen, and probably of phosphuretted hydrogen, but is itself very liable to change. Not only do its elements separate when electric sparks are passed through it, or by exposure to a strong heat, but it is apt to decompose spontaneously at common temperatures, whereby the same specimen may vary in composition during the interval of an hour. Rose, in his last essay, contends that the two compounds of phosphorus and hydrogen, are isomeric, being identical in composition, and differing in character only by one being spontaneously inflammable and the other not so.

SECTION VI.

COMPOUNDS OF NITROGEN AND CARBON.

BICARBURET OF NITROGEN, OR CYANOGEN GAS.

Cyanogen gas, the discovery of which was made in 1815 by Gay-Lussac, (An. de Ch. xcv.) is prepared by heating carefully dried bicyanuret of mercury in a small glass retort by means of a spirit-lamp. This cyanuret, which was formerly considered a compound of oxide of mercury and prussic acid, and was then called *prussiate of mercury*, is composed of metallic mercury and cyanogen. On exposure to a low red heat, it is resolved into its elements; the cyanogen passes over in the form of gas, and the metallic mercury is sublimed. The retort, at the close of the process, contains a small residue of a dark brown matter like charcoal, but which Mr. Johnston has shown to consist of the same ingredients as the gas itself.

Cyanogen gas is colourless, and has a strong pungent and very peculiar odour. At the temperature of 45° and under a pressure of 3.6 atmospheres, it is a limpid liquid, which Mr. Kemp finds to be a non-conductor of electricity, and which resumes the gaseous form when the pressure is removed. It extinguishes burning bodies; but it is inflammable, and burns with a beautiful and characteristic purple flame. It can support a strong heat without decomposition. Water, at the temperature of 60° absorbs 4.5 times, and alcohol 23 times its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water. It appears from the observations of Wöhler that two of the products are cyanic acid and ammonia; which, uniting together, generate urea. (An. de Ch. et de Ph. xliii. 73.)

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

	Grains.
100 cubic inches of nitrogen gas weigh	30.1650
200 do. the vapour of carbon weigh .	26.1428
100 cubic inches of cyanogen gas must weigh . .	56.3078

The ratio of its elements by weight is

Nitrogen .	30.1650 .	0.9727 . .	14.15	1 eq.
Carbon .	26.1428 .	0.8430 (2×0.4215)	12.24	2 eq.

The specific gravity of a gas so constituted is $0.9727+0.843=1.8157$, which is near 1.8064, the number found experimentally by Gay-Lussac.

Cyanogen is a *bicarburet of nitrogen*, the formula of which is $N+2C$ or NC^2; but its most convenient name is *cyanogen*, proposed by its discoverer,* which may be expressed shortly by Cy.

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evinces a strong attraction for metals. When potassium, for instance, is heated in cyanogen gas, such energetic action ensues, that the metal becomes incandescent, and cyanuret of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid.

An examination of the brown matter, left in the retort after the preparation of cyanogen gas, has been made by Mr. Johnston, who by burning it with chlorate of potassa found it to contain carbon and nitrogen united in the same ratio as in cyanogen gas. It is, in fact, a solid bicarburet of nitrogen, isomeric with cyanogen, but differing from it essentially in its physical and chemical relations. On heating this solid bicarburet in the open air, several definite compounds of carbon and nitrogen may be successively obtained. After considerable heating, the ratio of carbon to nitrogen is as 3 to 2; again heated, the proportion becomes as 7 to 6; and finally, after a still longer heat, the ratio of the equivalents is as 1 to 1. Thus the carbon is gradually burned away, leaving the nitrogen fixed, until a protocarburet of nitrogen is formed. On continuing the heat after this period, both elements fly off together, and the whole is dissipated. The solid bicarburet of cyanogen is also generated, when a saturated solution of cyanogen in alcohol is kept in contact with mercury; and Mr. Johnston suggests that the carbonaceous residue after the charring of animal substances by heat, is probably in many cases a carburet of nitrogen, and not pure charcoal as is commonly thought. (Brewster's Journ. N. S. i. 75.)

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* From *κύανος blue*, and *γεννάω I generate;* because it is an essential ingredient of Prussian blue.

The composition of the compounds of cyanogen described in this section isas follows:—

	Cyanogen.						Equiv.	Formulæ.
Hydrocyanic acid	26.39	1 eq.+	Hydrogen	1	1 eq.	=	27.39	$H+Cy$
Cyanic acid .	26.39	1 eq.+	Oxygen	8	1 eq.	=	34.39	$Cy+O$
Fulminic (cyanic) acid	26.39	1 eq.+	do.	8	1 eq.	=	34.39	$Cy+O$
Cyanuric acid Paracyanuric acid	79.17	3 eq.+	Oxygen Hydrog.	48 3	6 eq. 3 eq.	=	130.17	$Cy^3O^6H^3$
Chloride of cyanogen . .	26.39	1 eq.+	Chlorine	35.42	1 eq.	=	61.81	$Cy+Cl$
Bichloride of cyanogen? .	26.39	1 eq.+	do.	70.84	2 eq.	=	97.23	$Cy+2Cl$
Iodide of cyanogen.	Composition uncertain.							
Bromide of cyanogen . .	Composition uncertain.							
Hydrosulphocyanic acid { Cyanogen Sulph.	26.39 32.2	1 eq. 2 eq.	+Hydr.	1	1 eq.	=	59.59	$H+CyS^2$
Bisulphuret of cyanogen .	26.39	1 eq.+	Sulphur	32.2	2 eq.	=	58.59	$Cy+2S$
Sulphuret of cyanogen .	Existence doubtful.							
Cyano-hydrosulphuric acid	26.39	1 eq.+	Sulphur Hydrog.	32.2 2	2 eq. 2 eq.	=	60.59	$Cy+2HS$? $2H+CyS^2$
Hydroseleniocyanic acid .	Composition uncertain.							

HYDROCYANIC OR PRUSSIC ACID.

This acid was discovered in the year 1782 by Scheele, and Berthollet afterwards ascertained that it contains carbon, nitrogen, and hydrogen; but Gay-Lussac first procured it in a pure state, and by the discovery of cyanogen was enabled to determine its real nature. The substance prepared by Scheele was merely a solution of hydrocyanic acid in water.

Pure hydrocyanic acid may be prepared by heating bicyanuret of mercury in a glass retort with two-thirds of its weight of concentrated hydrochloric acid. By an interchange of elements

2 eq. hydrochloric acid and 1 eq. bicyanuret of mercury,
$2(H+Cl)$ $Hg+2Cy$,

yield

2 eq. hydrocyanic acid and 1 eq. bichloride of mercury.
$2(H+Cy)$ $Hg+2Cl$.

The volatile hydrocyanic acid passes off in vapour along with moisture and hydrochloric acid: by transmission through a tube over fragments of marble it is deprived of hydrochloric acid. It is then dried by passing through another tube filled with fused chloride of calcium in fragments, and is ultimately collected in a clean dry tube surrounded by ice.

Vauquelin proposes the following process, which affords a more abundant product than the preceding. It consists in filling a narrow tube, placed horizontally, with fragments of bicyanuret of mercury, and causing a current of dry hydrosulphuric acid gas to pass very slowly along it. The instant that gas comes in contact with the bicyanuret, double decomposition ensues, and hydrocyanic acid and bisulphuret of mercury are generated. The progress of the hydrosulphuric acid along the tube may be distinctly traced by the change of colour, and the experiment should be closed as soon as the whole of the bicyanuret has become black. It then only remains to expel the hydrocyanic acid by a gentle heat, and collect it in a cool receiver. This process is elegant, easy of execution, and productive.

Pure hydrocyanic acid is a limpid colourless fluid, of a strong odour, similar to that of peach blossoms. It excites at first a sensation of coolness on the tongue, which is soon followed by heat; but when diluted, it has the flavour of bitter almonds. Its specific gravity at 45° is 0.7058. It is so exceedingly volatile that its vapour during warm weather may be collected over mercury. Its point of ebullition is 79°, and at zero it congeals. When a drop of it is placed on a piece of glass, it becomes solid, because the cold produced by the evaporation of one portion is so great as to freeze the remainder. It unites with water and alcohol in every proportion.

Pure hydrocyanic acid is a powerful poison, producing in poisonous doses insensibility and convulsions, which are speedily followed by death. A single drop of it placed on the tongue of a dog causes death in the course of a very few seconds; and small animals, when confined in its vapour, are rapidly destroyed. On inspiring the vapour, diluted with atmospheric air, headach and giddiness supervene; and for this reason the pure acid should not be made in close apartments during warm weather. The distilled water from the leaves of the *Prunus lauro-cerasus* owes its poisonous quality to the presence of this acid. Its effects are best counteracted by diffusible stimulants, and of such remedies solution of ammonia appears to be the most beneficial. The aqueous solution of chlorine may be used as an antidote, which decomposes hydrocyanic acid instantly, with formation of hydrochloric acid. In some experiments, recently described by MM. Persoz and Nonat, symptoms of poisoning, induced by hydrocyanic acid applied to the globe of the eye, ceased on the internal administration of chlorine. It would hence appear, that both substances were absorbed into the circulating fluids, and there reacted on each other. (An. de Ch. et de Ph. xliii. 324.)

Pure hydrocyanic acid, even when excluded from air and moisture, is very liable to spontaneous changes, owing to the tendency of its elements to form new combinations. These changes sometimes commence within an hour after the acid is made, and it can rarely be preserved for more than two weeks. The commencement of decomposition is marked by the liquid acquiring a reddish-brown tinge. The colour then gradually deepens, a matter like charcoal subsides, and ammonia is generated. On analyzing the black matter, it was found by Gay-Lussac to contain carbon and nitrogen: M. P. Boullay considers it to be a peculiar acid, composed of carbon, nitrogen, and hydrogen, very analogous to ulmic acid, and for which he proposes the name of *azulmic acid;* but farther observation is desirable before this view can be relied on. Hydrocyanic acid may be preserved for a longer period if diluted with water, but even then it undergoes gradual decomposition.

Hydrocyanic acid is one of the feeblest of the acids. It is not acid to the taste, scarcely reddens litmus paper, does not decompose the salts of carbonic acid, and is unable in any quantity to neutralize the alkaline reaction of potassa. When mixed with metallic oxides it rarely if ever enters into combination, so as to constitute hydrocyanates; but by an interchange of elements, water and metallic cyanurets are generated. Though a solution of cyanuret of potassium is alkaline, has the odour of hydrocyanic acid, and acts like that acid as a poison, it does not follow that potassa and hydrocyanic acid were in combination; for they may be merely developed at the moment by the influence of carbonic acid of the air, or of any substance which has an affinity for potassa.

Hydrocyanic acid is resolved by galvanism into hydrogen and cyanogen, the former of which appears at the negative and the latter at the positive pole. When its vapour is conducted through a red-hot porcelain tube, partial decomposition ensues. Charcoal is deposited, and nitrogen, hydrogen, and cyanogen gases are set at liberty; but the greater part of the acid passes over unchanged. Electricity produces a similar effect. The vapour of hydrocyanic acid takes fire on the approach of flame; and with oxygen gas it forms a mixture which detonates with the electric spark. The products of the combustion are nitrogen, water, and carbonic acid.

Gay-Lussac proved that hydrocyanic acid vapour is analogous in composition to hydrochloric acid gas, consisting of equal measures of cyanogen and hydrogen gases united without change of volume; for on heating potassium in 100 measures of hydrocyanic acid vapour, he obtained as much cyanuret of potassium as would have been formed from 50 measures of cyanogen gas, and 50 measures of pure hydrogen remained. Hence, as

			Grains.
50	cubic inches of	cyanogen gas weigh . . .	28.1539
50	do.	hydrogen gas	1.0683
100	do.	hydrocyanic acid vapour should weigh	29.2222

Also 1.0683 is to 28.1539 as 1 to 26.39, the composition given in the table. The density of a gas so constituted should be $\frac{1}{2}(1.8157 + 0.069) = 0.9423$; whereas the number which Gay-Lussac found by weighing the gas is 0.9476.

From the powerful action of hydrocyanic acid on the animal economy, this substance, in a diluted form, is sometimes employed in medical practice to diminish pain and nervous irritability. Several processes are in use for obtaining the medicinal acid of uniform strength and of a quality to keep long without decomposition.

I. One of these consists in transmitting a current of hydrosulphuric acid gas through water, holding in solution a known weight of bicyanuret of mercury, until *complete* decomposition, which is ascertained by the filtered liquid remaining colourless when acted on by an additional quantity of hydrosulphuric acid. The excess of this acid is removed by agitation with carbonate of oxide of lead, after which the solution is filtered.—It admits of doubt whether the hydrocyanic acid thus obtained is uniform; since a quantity of its vapour, variable in different operations, is apt to be carried off by the hydrosulphuric acid gas.

II. Another process, adopted at Apothecaries' Hall, is to mix in a retort 1 part of bicyanuret of mercury, 1 part of hydrochloric acid of sp. gravity 1.15, and 6 parts of water; and to distil the mixture until a quantity of acid, equal to that of the water employed, is collected. The product has a density of 0.995. (Brande's Chemistry). A little hydrochloric acid commonly passes over into the recipient, and may be got rid of and discovered by mixing the impure acid with a little chalk and distilling to dryness, when chloride of calcium remains. Its presence while mixed with hydrocyanic acid cannot well be detected by nitrate of oxide of silver; because cyanuret of silver is very similar to the chloride both in appearance, and in several of its leading properties. The cyanuret, however, is soluble in hot nitric acid, and yields cyanogen gas when heated to redness, by which characters it may be distinguished from chloride of silver. In a medicinal point of view the presence of a little hydrochloric acid is not material, and tends probably to give greater stability to the product than it would possess if absolutely pure.

III. A third and very good process is that recommended by Dr. Clark, who mixes solutions of cyanuret of potassium and tartaric acid in such proportions as to form bitartrate of potassa and hydrocyanic acid. In 100 drachms of water are dissolved 8¼ of cyanuret of potassium, and with this is mixed a solution of 18¾ drachms of crystallized tartaric acid in 20 of water; and after the sparingly soluble bitartrate of potassa has subsided, the clear solution is decanted for use. Its only impurity is a little bitartrate, the presence of which in a medicinal point of view is not objectionable. The oxygen and hydrogen, which unite with the elements of the cyanuret of potassium, are derived from decomposed water. Mr. Laming adds to the preceding materials a portion of alcohol, which tends to promote the separation of bitartrate of potassa, and perhaps to preserve the hydrocyanic acid from change.

IV. In a fourth process 20 drachms of pulverized ferrocyanuret of potassium are dissolved in 80 of water; and with this solution is mixed a dilute acid made previously with 18 drachms (by weight) of strong sulphuric acid and 40 drachms of water, and allowed to cool. The dilute hydrocyanic acid is then obtained by distillation, gentle ebullition being continued until the materials become rather thick, and strong succussions commence. If the amount distilled over does not weigh 120 drachms, the requisite quantity of distilled water should be added to give that weight. The foregoing proportions are recommended by Giese, who states that the acid so prepared may be kept for years. Dr. Christison tells me he has had some unchanged for 2½ years, though exposed to diffused daylight; and that it contains a small quantity of sulphuric acid, which is probably the preservative agent. The process ought to be conducted in a capacious matrass instead of a retort; as when the last is used, a little Prussian blue is apt to pass over. The production of hydrocyanic acid in the foregoing process is due to cyanogen uniting with the hydrogen, and potassium uniting with the oxygen of water, a change which is determined by the affinity of sulphuric acid for potassa; but besides hydrocyanic acid and sulphate of potassa, the colouring principle called *Prussian blue* is generated.

As the quality of dilute hydrocyanic acid, however prepared, is apt to vary, owing to the volatility of the acid, and its tendency to spontaneous decomposition, it should be made only in small quantities at a time, kept in well-stopped bottles, and excluded from light. One of the best modes of estimating the strength of any solution, as Orfila suggests, is by precipitation with nitrate of oxide of silver. The cyanuret, after being washed and moderately dried, consists of 108 parts of silver and 26.39 of cyanogen, being an equivalent of each; and, therefore, 100 parts of the dry cyanuret correspond to 20.9 of real hydrocyanic acid.

M. Pelouze has noticed that when strong hydrocyanic and hydrochloric acids are mixed together, the whole shortly becomes a solid saline mass, from which a gentle heat expels formic acid, while hydrochlorate of ammonia remains behind. The hydrocyanic acid, by the aid of water, is entirely resolved into ammonia and formic acid; and hydrochloric acid appears to determine the change by its affinity for ammonia. Thus

1 eq. hydrocyanic acid and 3 eq. water yield 1 eq. ammonia and 1 eq. formic acid.

$$H+(N+2C) \qquad 3(H+O) \qquad 3H+N \qquad 2(C+O)+(H+O).$$

Sulphuric acid acts on hydrocyanic acid in the same manner as the hydrochloric; but it is apt to decompose the formic acid. It was also observed that when cyanuret of potassium is boiled in pure water, hydrocyanic acid disappears, ammonia is disengaged, and formate of potassa is left in solution: thus are the same changes determined by the affinity of potassa for formic acid, as by that of hydrochloric acid for ammonia. (An. de Ch. et de Ph. xlviii. 395.)

The presence of free hydrocyanic acid is easily recognized by its odour. Chemically it may be detected by agitating the fluid supposed to contain it with peroxide of mercury in fine powder. Double decomposition ensues, by which water and bicyanuret of mercury are generated; and on evaporating the solution slowly, the latter is obtained in the form of crystals.

A test of far greater delicacy, originally noticed by Scheele, is the following. To the liquid supposed to contain hydrocyanic acid, add a solution of green vitriol, throw down the protoxide of iron by a slight excess of pure potassa, and acidulate with hydrochloric or sulphuric acid, so as to redissolve the precipitate. Prussian blue will then make its appearance, if hydrocyanic acid had been originally present. The nature of the chemical change will be explained in the section on the haloid salts when describing the manufacture of Prussian blue. The presence of *protoxide* of iron is essential.

As hydrocyanic acid is sometimes administered with criminal designs, the chemist may be called on to search for its presence after death. The subject has been investigated experimentally by Leuret and Lassaigne, and the process they have recommended is the following. The stomach or other substances to be examined are cut into small fragments, and introduced into a retort along with water, the liquid being slightly acidulated with sulphuric acid. The distillation is then conducted by the heat of boiling water, the volatile products are collected in a receiver surrounded with ice, and the presence of hydrocyanic acid in the distilled matter is tested by the method above mentioned. These gentlemen found that hydrocyanic acid may be thus detected two or three days after death, but not after a longer period. In the case of a young man poisoned during the winter season by a strong dose of the poison, I detected it four days after death; but the quantity obtained was very minute, though the odour of hydrocyanic acid emitted by the contents of the stomach was considerable. The disappearance of the acid appears owing partly to its volatility, and partly to the facility with which it undergoes spontaneous decomposition. (Journal de Chimie Medicale, ii. 561.)

Cyanic Acid.—There are two compounds entitled to this appellation, one of which was discovered by Wöhler and the other by Liebig; but to prevent confusion I shall apply to the former the term *cyanic acid*, and that of *fulminic acid* to the latter.

It was stated by Gay-Lussac, in the essay already quoted, that cyanogen gas is freely absorbed by pure alkaline solutions; and he expressed his opinion that the alkali combines directly with the cyanogen. It appears, however, from the experiments of Wöhler, that cyanic acid and a cyanuret are formed under these circumstances; and, consequently, that alkaline solutions act upon cyanogen in the same manner as on chlorine, iodine, bromine, and sulphur. But the salts of cyanic acid cannot conveniently be procured in this way, owing to the difficulty of separating the cyanate from the cyanuret with which it is accompanied. Wöhler finds that cyanate of potassa may be procured in large quantity by mixing ferrocyanuret of potassium with an equal weight of peroxide of manganese in fine powder, and exposing the mixture to a low red heat. The cyanogen and potassium of that salt receive oxygen from the manganese, and are converted into cyanate of potassa. The ignited mass is then boiled in alcohol of 86 per cent; and as the solution cools, the cyanate is deposited in small tabular crystals resembling chlorate of potassa. The only precaution necessary in this process is to avoid too high a temperature.

Cyanic acid is characterized by the facility with which it is resolved by water into carbonic acid and ammonia. This change is effected merely by boiling an aqueous solution of cyanate of potassa; and it takes place still more rapidly when an attempt is made to decompose the cyanate by means of another acid. If the acid is diluted, cyanic acid is instantly decomposed, and carbonic acid escapes with effervescence. But, on the contrary, if a concentrated acid is employed, then the cyanic acid resists decomposition for a short time, and emits a strong odour of vinegar. Wöhler and Liebig have succeeded in obtaining it in a very concentrated and pure state by placing cyanuric acid, previously deprived of its water of crystallization by a temperature of 212°, in a small glass retort, and applying a heat gradually increasing to low redness. The vapours are collected in a receiver surrounded by a freezing mixture of salt and ice, and are thereby condensed into a limpid colourless liquid, which was at first supposed to be anhydrous cyanic acid, but which turns out to be cyanic acid with one equivalent of water. This liquid has a penetrating odour similar to the strongest acetic acid, is extremely pungent, produces a flow of tears, and when applied in minute quantity to the skin instantly causes a white vesicle to be formed, attended with severe pain. It is very volatile, giving off a vapour which is inflammable, and has a strong acid reaction. When this vapour is conducted into ice-cold water, it is freely dissolved without decomposition; but as soon as the temperature rises a little, carbonic acid escapes with effervescence, and the acid is entirely destroyed. When the pure hydrous acid, removed from the freezing mixture, has acquired the temperature of the air, it speedily begins to grow turbid, its temperature rises, and the liquid enters into violent ebullition from the heat vaporizing the acid. During this action no gas whatever is evolved; but a white insoluble substance is rapidly produced, and in the course of a few minutes the whole liquid acid entirely disappears, and a dry compact matter of brilliant whiteness occupies its place. This solid will hereafter be alluded to under the name of *insoluble cyanuric acid*, when it will be found to contain precisely the same elements as the hydrous cyanic acid.

The composition of cyanic acid, as stated at page 266, has been fully established by Wöhler and Liebig. (An. de Ch. et de Ph. xx. and xxvii.) It will be understood, from the ratio of its elements and their known affinities, why a solution of cyanic acid in water is readily convertible into bicarbonate of ammonia; for one equivalent of cyanic acid with three equivalents of water contain exactly the same elements as one equivalent of bicarbonate of ammonia: Thus

1 eq. cyanic acid and	3 eq. water.		2 eq. carbonic acid and	1 eq. ammonia.
$(N+2C)+O$	$3(H+O)$	yield	$2(C+2O)$	$3H+N.$

A great part of the carbonic acid is disengaged in a free state, because the bicarbonate formed by one portion of cyanic acid is decomposed by another; so that cyanate of ammonia (urea) is instantly generated, and remains in solution. It is also obvious that pure hydrous cyanic acid cannot undergo the same change as its aqueous solution.

Cyanic acid forms a soluble salt with baryta, but insoluble ones with the oxides of lead, mercury, and silver. A pure soluble cyanate, as that of potassa for instance, gives a white precipitate with nitrate of oxide of silver; and the cyanate of that oxide is soluble without residue in dilute nitric acid. The action of cyanic acid on ammonia is peculiarly interesting. When dry ammoniacal gas is mixed with the vapour of hydrous cyanic acid, they form a white crystalline salt, which is a cyanate of ammonia with excess of alkali, probably a dicyanate, and one equivalent of water. This salt dissolves in water, and possesses all the characters of a cyanate of ammonia: potassa displaces ammonia, and an acid expels cyanic acid. But on applying a gentle heat to the dry salt, or evaporating its aqueous solution, ammonia escapes, and a substance remains composed of the same elements as cyanic acid and ammonia, but which does not evolve cyanic acid or ammonia when an acid or alkali is added; and in which all the properties of the animal principle urea may be recognized. The possibility of such a change is readily understood by comparing the composition of urea, and that of cyanate of ammonia with one equivalent of water.—Thus

Carbon	12.24	2 eq.	Urea.	Cyanic acid	34.39	1 eq.	$(N+2C)+O.$
Nitrogen	28.3	2 eq.		Ammonia	17.15	1 eq.	$3H+N.$
Hydrogen	4	4 eq.		Water	9	1 eq.	$H+O.$
Oxygen	16	2 eq.			60.54		
	60.54						

The hydrated neutral cyanate of ammonia has exactly the same ingredients and the same equivalent as urea; and whenever the elements for producing the former come into contact, they invariably constitute the latter. This production of urea ensues so readily, that mere exposure of the dry dicyanate to the air, or the spontaneous evaporation of its aqueous solution.

suffices for the change. These phenomena illustrate in a most instructive manner the subject of isomerism, and prove how possible it may be, by a difference in arrangement, to produce two different compounds with the same materials. (An. de Ch. et de Ph. xlvi. 25.)

The existence of cyanic acid was suspected by Vauquelin before it was actually discovered by Wöhler. The experiments of the former chemist led him to the opinion that a solution of cyanogen in water is gradually converted into hydrocyanic, cyanic, and carbonic acids, and ammonia; and he supposed alkalies to produce a similar change. He did not establish the fact, however, in a satisfactory manner. (An. de Ch. et de Ph. vol. ix.)

Fulminic Acid.—A powerfully detonating compound of mercury was described in the Philosophical Transactions for 1800 by Mr. E. Howard. It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid of specific gravity 1.3; and adding, when the solution has become cold, two ounces by measure of alcohol, the density of which is 0.849. The mixture is then heated till moderately brisk effervescence takes place, during which the fulminating compound is generated. A similar substance may be made by treating silver in the same manner. The conditions necessary for forming these compounds are, that the silver or mercury be dissolved in a fluid which contains so much free nitric acid and alcohol, that on the application of heat nitric ether shall be freely disengaged.

Fulminating silver and mercury bear the heat of 212° or even 260° without detonating; but a higher temperature, or slight percussion between two hard bodies, causes them to explode with violence. The nature of these compounds was discovered in 1823 by Liebig,* who demonstrated that they are salts composed of a peculiar acid, which he termed *fulminic acid*, in combination with oxide of mercury or silver. According to an analysis of fulminating silver made by Liebig and Gay-Lussac,† the acid of the salt is composed of 26.39 parts or one equivalent of cyanogen, and 8 parts or one equivalent of oxygen. It is hence inferred to be a real *cyanic acid*, identical in composition with the cyanic acid of Wöhler, though essentially different in its properties. The composition of this acid is differently stated by Mr. Davy of Dublin; but the known care and skill of Gay-Lussac and Liebig in such researches justify all confidence in their result.

It is remarkable that the oxide of silver cannot be entirely separated from fulminic acid by means of an alkali. On digesting fulminate of that oxide in potassa, one equivalent of oxide of silver is separated, and a double fulminate is formed, which consists of two equivalents of fulminic acid, one of oxide of silver, and one of potassa. Similar compounds may be procured by substituting other alkaline substances, such as baryta, lime, or magnesia, for the potassa. These double fulminates are capable of crystallizing; and they all possess detonating properties.

From the presence of oxide of silver in the double fulminates, it was at first imagined that this oxide actually constitutes a part of the acid; but since several other substances, such as oxide of mercury, zinc, and copper, may be substituted for that of silver, this view can no longer be admitted.

We are indebted to Mr. Davy for a method of obtaining fulminic acid in a separate state. Into a bottle with a ground stopper are inserted one part of fulminating mercury, two parts of clean zinc filings, and about 18 parts of water; and the materials, kept at a temperature of 80°, are occasionally agitated, in order that metallic mercury should be thrown down and fulminate of oxide of zinc be generated. This salt is then decomposed by a solution of pure baryta, and the resulting fulminate of baryta decomposed by a quantity of dilute sulphuric acid just sufficient to neutralize the baryta. The fulminic acid thus obtained is a colourless, transparent liquid, of a pungent odour, somewhat like strong prussic acid, and has a sweet taste followed by a particular astringency and disagreeable impression on the palate. It is volatile, poisonous to animals, and has an acid reaction. After a few hours it acquires a yellow tint, and undergoes partial decomposition; but the nature of the change, and the effects of heat and chemical agents in general on fulminic acid are not yet understood.

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* An. de Ch. et de Ph. vol. xxiv. † Ibid. xxv.

Cyanuric Acid.—This compound was originally prepared by gently boiling the so-called bichloride of cyanogen in water. On the supposition of its discoverer Serullas, that it consists solely of cyanogen and oxygen, and that his bichloride of cyanogen has the composition implied by its name, the origin of cyanuric acid would be referable to the mutual decomposition of water and the bichloride; but since Wöhler and Liebig have proved cyanuric acid to contain hydrogen as well as oxygen and cyanogen, its production by this method ceases to be intelligiblo, and there is consequently a well-grounded suspicion of the bichloride of cyanogen having a different constitution from that stated by Serullas. (An. de Ch. et de Ph. xxxviii. 379, and xlvi. 25.) However this may be, the preceding process gives rise to cyanuric and hydrochloric acids; and on evaporating the solution, the latter is expelled in vapour, and the former deposited on cooling in oblique rhomboidal prisms. The crystals are further purified by a second solution and evaporation.

As thus obtained, cyanuric acid is chemically united with two equivalents of water. The recent crystals are colourless and transparent, but become opaque by exposure to the air, and if heated to 212°, their water of crystallization is wholly expelled. In cold water they are very sparingly soluble; but they are dissolved by this menstruum, as also by sulphuric, nitric, and hydrochloric acid, with the aid of heat. They have little taste, redden litmus paper, and are rather lighter than sulphuric acid. One of the most remarkable characters of the acid is its permanence. For instance, it may be boiled in strong nitric or sulphuric acid without decomposition; and by evaporating its solution in the former, it is obtained in a very white and pure state. It is volatile at a lower temperature than boiling mercury, and condenses, unchanged, in the form of acicular crystals. When heated with potassium, it is decomposed, yielding potassa and cyanuret of potassium. With metallic oxides it forms permanent salts, which do not detonate.

Anhydrous cyanuric acid, first noticed by Wöhler, is obtained by cooling from a hot concentrated solution of the crystals in sulphuric or hydrochloric acid. The figure of its crystals, when they are regularly formed, is that of an octohedron with a square base. When the anhydrous acid is sharply heated, part of it sublimes without change; but part is decomposed, and hydrous cyanic acid, as already mentioned, is formed in considerable quantity.

Liebig and Wöhler have remarked, that the substance called pyro-uric acid, which sublimes when uric acid is decomposed by heat, is cyanuric acid. This compound is also formed, according to Liebig, by transmitting chlorine gas through water in which cyanate of oxide of silver is suspended; chloride of silver, carbonic acid, and ammonia being generated at the same time. Liebig also states, that on heating dry uric acid in dry chlorine gas, a large quantity of cyanic and hydrochloric acids is generated. He adds, further, that cyanate of potassa, when heated in strong acetic acid, is converted into cyanurate of potassa. (An. de Ch. et de Ph. xli. 225, and xliii. 64.)

Cyanuric acid may also be obtained from urea, a mode of preparation which has lately been illustrated by the joint labours of Wöhler and Liebig. When pure urea is put into a retort, and heated by a gradually increasing temperature to about 600°, it is entirely resolved into ammonia and anhydrous cyanuric acid, the former of which escapes, while the latter, if the heat be carefully managed, is left entirely in the retort. In order to separate some ammonia which is always retained, it is dissolved in hot concentrated sulphuric acid, and nitric acid is added drop by drop until it occasions no further effervescence, and the solution becomes colourless. After cooling it is mixed with cold water, which throws down the cyanuric acid in the form of a crystalline powder of brilliant whiteness. It may also be purified by transmitting a current of chlorine through water in which the impure acid is suspended. Very large crystals may be obtained by forming a saturated solution of the pure acid in boiling water, evaporating it to one-half of its volume on a sand-bath heated to about 150°, and allowing it to cool gradually on the sand-bath itself.

The analysis of cyanuric acid by Wöhler and Liebig accounts in an elegant manner for its production from urea. They have established the singular fact that cyanuric acid contains the same elements, in the very same proportion, as hydrous cyanic acid. Hence the formulæ of page 271, connecting the composition of urea and hydrous cyanic acid, will also serve to compare the constitution of urea and cyanuric acid: the elements of urea may be disposed into such order as to constitute either hydrated cyanate, or anhydrous cyanurate, of ammonia, though in reality they have, doubtless, a very different arrangement. The elements of water, contained in hydrous cyanic acid as water, and separable from that acid, appear to exist in cyanuric acid in a wholly different state, and to be essential to the existence of cyanuric acid. Besides, one equivalent of cyanuric acid (page 266), namely, 3Cy, 6O, and 3H, contains the same elements as three equivalents of hydrous cyanic acid; and hence three eq. of urea are capable of supplying one eq. of cyanuric acid and three eq. of ammonia.

Another interesting compound described in the important essay of Wöhler and Liebig, is that which they have termed *insoluble cyanuric acid*, a compound entirely different in its chemical properties from the preceding soluble acid, and yet identical with it in the nature and ratio of its elements, and in having the same equivalent. This is the substance already mentioned as the sole product of the spontaneous decomposition of hydrous cyanic acid, three eq. of which yield one eq. of insoluble cyanuric acid, without loss or gain of a single element. This acid, as isomeric with cyanuric acid, may appropriately be called *paracyanuric acid*.

The preceding history sufficiently explains the origin of the name applied to these acids. The term *cyan-uric*, is suggested by the close relation of these acids to urea and uric acid, added to the circumstance of cyanogen being an essential part of their composition.

Chloride of Cyanogen.—The existence of this compound was first noticed by Berthollet, who named it *oxyprussic acid*, on the supposition of its containing prussic acid and oxygen; and it was afterwards described by Gay-Lussac, in his essay on cyanogen, under the appellation of *chlorocyanic acid*. It was procured by this chemist by transmitting chlorine gas into an aqueous solution of hydrocyanic acid until the liquid acquired bleaching properties, removing the excess of chlorine by agitation with mercury, and then heating the mixture, so as to expel the gaseous chloride of cyanogen. The chemical changes which take place during this process are complicated. At first the elements of hydrocyanic acid unite with separate portions of chlorine, and give rise to hydrochloric acid and chloride of cyanogen; and when heat is applied, the elements of the chloride and water react on each other, in consequence of which hydrochloric acid, ammonia, and carbonic acid are generated. Owing to this circumstance the chloride of cyanogen was always mixed with carbonic acid, and its properties imperfectly understood.

During the year 1829 Serullas succeeded in procuring this compound in a pure state, by exposing bicyanuret of mercury, in powder and moistened with water, to the action of chlorine gas contained in a well-stopped phial. The vessel is kept in a dark place; and after ten or twelve hours the colour of the chlorine is no longer perceptible, bichloride of mercury is found at the bottom of the phial, and its space is filled with the vapour of chloride of cyanogen. The bottle is then cooled down to zero by freezing mixtures of snow and salt, at which temperature chloride of cyanogen is solid. Some chloride of calcium is then introduced, the stopper replaced, and the bottle kept in a moderately warm situation, in order that the moisture within may be completely absorbed. The chloride of cyanogen is then again solidified by cold, the phial completely filled with dry and cold mercury, and a bent tube adapted to its aperture by means of a cork. The solid chloride, which remains adhering to the inner surface of the phial, is converted into gas by gentle heat, and passing along the tube, is collected over mercury. Exposure to the direct solar rays interferes with the success of this process: hydrochlorate of ammonia, together with a little carbonic acid, is then generated, and a yellow liquid collects, which appears to be a mixture of chloride of carbon and chloride of nitrogen. (An. de Ch. et de Ph. xxxv. 291.)

Chloride of cyanogen is solid at 0°, and in congealing crystallizes in very long slender needles. At temperatures between 5° and 10.5° it is liquid, and also at 68° under a pressure of four atmospheres; but at the common pressure, and when the thermometer is above 10.5° or 11°, it is a colourless gas. In the liquid state it is as limpid and colourless as water, It has a very offensive odour, irritates the eyes, is corrosive to the skin, and highly injurious to animal life.

Chloride of cyanogen is very soluble in water and alcohol. The former under the common pressure, and at 68° dissolves twenty-five times its volume. Alcohol takes up 100 times its volume, and the absorption is effected almost with the same velocity as that of ammoniacal gas by water. These solutions are quite neutral with respect to litmus and turmeric paper, and may be kept without apparent change. The gas may even be separated without decomposition by boiling. The chloride of cyanogen, accordingly, does not possess the characters of an acid.

The changes induced by the action of alkalies do not appear to be very clearly understood. Serullas agrees with Gay-Lussac in stating, that if to a solution of chloride of cyanogen a pure alkali is added, and then an acid, effervescence ensues from the escape of carbonic acid gas. Ammonia, and probably hydrochloric and hydrocyanic acid, are also generated.

According to Gay-Lussac and Serullas, 100 measures of the vapour of chloride of cyanogen contain 50 measures of cyanogen and 50 of chlorine gases. The density of a vapour so constituted should be 2.1428 and its elements have the ratio assigned at page 266.

Bichloride of Cyanogen.—This compound, which is said to contain twice as much chlorine as the preceding, was prepared by Serullas by the action of dry chlorine on anhydrous hydrocyanic acid, hydrochloric acid being generated at the same time. It is solid at common temperatures, and occurs in white acicular crystals. At 284° it fuses, and enters into ebullition at 374°. Its vapour is acrid and excites a flow of tears, and it is very destructive to animals. Its odour somewhat resembles that of chlorine, and is very similar to that of mice. It is very soluble in alcohol and ether, and is precipitated from them by water, which dissolves it in small quantity. When boiled in water, or solution of potassa, it is converted into hydrochloric and cyanuric acids. (An. de Ch. et de Ph. xxxviii. 370.) Recent researches throw great doubt on the composition of this substance as stated by Serullas. (Page 273.)

Iodide of Cyanogen.—This compound was discovered by Davy in 1816. (Quarterly Journal of Science, i. 289.) and since studied by Serullas, who recommended for its preparation the following process. (An. de Ch. et de Ph. xxvii.) Two parts of bicyanuret of mercury and one of iodine are intimately and quickly mixed in a glass mortar, and the mixture is introduced into a phial with a wide mouth. On applying heat the violet vapours of iodine appear; but as soon as the bicyanuret of mercury begins to be decomposed, the vapour of iodine is succeeded by white fumes, which, if received in a cool glass receiver, condense upon its sides into flocks like cotton wool. The action is found to be promoted by the presence of a little water.

Iodide of cyanogen, when slowly condensed, occurs in very long and exceedingly slender needles, of a white colour. It has a very caustic taste and penetrating odour, and excites a flow of tears. It sinks rapidly in sulphuric acid. It is very volatile and sustains a temperature much higher than 212° without decomposition, but it is decomposed by a red heat. It dissolves in water and alcohol, and forms solutions which do not redden litmus paper.

s act upon it in the same manner as on chloride of cyanogen, a com- to which it is very analogous.

hurous acid, when water is present, has a very powerful action on of cyanogen. On adding a few drops of this acid, iodine is set free, drocyanic acid produced; but when more of the sulphurous acid is red, the iodine disappears, and the solution is found to contain hy- acid. These changes are of course accompanied with formation of ric acid, and decomposition of water.

de of cyanogen has not been analyzed with accuracy; but Serullas in- m an approximate analysis, that it is composed of one equivalent of and one of cyanogen.

nide of Cyanogen.—This substance was prepared by Liebig by a pro- milar to that described for procuring iodide of cyanogen. At the bot- a small tubulated retort, or a rather long tube, is placed some bicy- of mercury slightly moistened, and after cooling the apparatus by ater, or still better by a freezing mixture, a precaution which is indis- le in summer, half its weight of bromine is introduced. Strong reac- stantly ensues, and heat is so freely evolved, that a considerable quan- the bromine would be dissipated, unless the temperature of the retort en previously reduced. The new products are bromide of mercury omide of cyanogen, the latter of which collects in the upper part of e in the form of long needles. After allowing any vapour of bromine, may have risen at the same time, to condense and fall back upon the uret of mercury, the bromide of cyanogen is expelled by a gentle nd collected in a recipient carefully cooled.

hus formed, the bromide is crystallized, sometimes in small regular ess and transparent cubes, and sometimes in long and very slender . In its physical properties it is so very similar to iodide of cyanogen, ey may easily be mistaken for each other, especially when the crys- the bromide possess the acicular form. They agree closely in odour latility, but the bromide is even more volatile than the iodide of cya- It is converted into vapour at 59°, and crystallizes suddenly on cool- ts solubility in water and alcohol is likewise greater than that of of cyanogen. By a solution of caustic potassa it is converted into of potassa and bromide of potassium.

ide of cyanogen is highly deleterious. A grain of it dissolved in a ater, and introduced into the œsophagus of a rabbit, proved fatal on ant, acting with the same rapidity as hydrocyanic acid. In conse- of the volatility and noxious qualities of the substance, experiments should be conducted with great circumspection. The danger from se, together with a deficient supply of bromine, prevented Serullas ontinuing the investigation of its properties. (Edin. Journal of vii. 189.)

sulphocyanic Acid.—This acid was discovered in 1808 by Mr. Por- ascertained that it is a compound of sulphur, carbon, hydrogen, ogen, and described it under the name of *sulphuretted chyazic acid*, *chyazic* being composed of the initials of carbon, hydrogen, and t is now generally called *sulphocyanic* or *hydrosulphocyanic acid.* be procured by distilling a strong solution of sulphocyanuret of n with phosphoric acid; when hydrosulphocyanic acid passes over ecipient, and phosphate of potassa remains in the retort: sulphuric be substituted for the phosphoric, but in that case sulphurous acid ted. Another process is to suspend recently formed sulphocyanuret or mercury in water, and transmit through it a current of hydro- acid gas; when, by an interchange of elements, sulphuret of silver y and hydrosulphocyanic acid are produced. The solution is fil- the excess of gas expelled by a gentle heat, or a small quantity of nuret of silver. (Berzelius.)

ution of hydrosulphocyanic acid is either colourless or has a shade nd its odour somewhat resembles that of vinegar. The strongest solution of it which Mr. Porrett could obtain had a sp. gravity of 1.022. At 216.5° it boils, and at 54.5° it crystallizes in six-sided prisms.

Though it contains the elements of hydrocyanic acid, it is quite distinct from it in its characters; it is much less poisonous, is distinctly acid to the taste and test paper, and neutralizes alkalies. Like most of the hydracids, it refuses to unite with many of the metallic oxides, because its radical unites by preference with the metal, and its hydrogen with the oxygen of the oxides.

Hydrosulphocyanic acid is easily detected by a salt of the peroxide of iron, with which it gives a deep blood-red solution. With a salt of copper it yields a white precipitate, which is a sulphocyanuret of that metal. It is gradually deprived of its hydrogen by exposure to the atmosphere, and the same change is rapidly effected by chlorine or nitric acid, bisulphuret of cyanogen being precipitated.

The composition of this hydracid, as given at page 266, is on the authority of Porrett and Berzelius. (An. of Phil. xiii., and An. de Ch. et de Ph. xvi.)

Bisulphuret of Cyanogen.—This compound is the *base* or *radical* of hydrosulphocyanic acid, and was obtained in a separate state by Liebig. (An. de Ch. et de Ph. xli. 187.) It was prepared by exposing fused sulphocyanuret of potassium to a current of dry chlorine gas. Reaction readily ensued, and at first chloride of sulphur and bichloride of cyanogen distilled over; but at length a red vapour appeared, which collected as a red or orange-coloured substance in the upper part of the tube. In this state it contained some free sulphur, which was in a great measure removed by heating it in dry chlorine gas; when it acquired an orange tint, and in powder was yellow. It had then so nearly the constitution of bisulphuret of cyanogen, that there can be little doubt of its being such. When heated with potassium, the action is exceedingly violent, and three compounds, sulphocyanuret, sulphuret, and cyanuret of potassium are generated.

If a solution of hydrosulphocyanic acid is exposed to the air, a yellow matter gradually collects, which Wöhler conceived to be a compound of sulphur and hydrosulphocyanic acid, but which Liebig considers bisulphuret of cyanogen. It is formed freely by boiling sulphocyanuret of potassium with dilute nitric acid, the best proportions being 1 part of the salt, 3 of water, and 2 or 2.5 of nitric acid; for if the nitric acid be too strong or in too great excess, the yellow compound will not be formed. It is also generated by the action of chlorine on a strong solution of the salt. In fact, the oxygen of the air, nitric acid, and chlorine, act upon sulphocyanic acid in the same manner as on hydriodic and hydrosulphuric acids. The yellow matter retains water with obstinacy.

Cyano-hydrosulphuric Acid.—When hydrosulphuric acid gas is transmitted into a saturated solution of cyanogen in alcohol, the liquid acquires a reddish-brown tint, and in a short time numerous small crystals of an orange-red colour are generated. At page 266 I have represented this acid as a compound of cyanogen with hydrosulphuric acid; but Wöhler and Liebig, who analyzed it, consider it rather as a hydracid differing from the hydrosulphocyanic, only in containing two equivalents of hydrogen instead of one. The red crystals consist of three eq. of the acid and one eq. of water, and dissolve in alcohol and water at a boiling temperature, but are sparingly soluble in both liquids when cold. The acid appears to unite directly with some metallic oxides; but with others a sulphocyanuret is formed. Frequently, as with acetate of oxide of lead, a sulphuret and sulphocyanuret of the metal are formed at the same time. (An. de Ch. et de Ph. xlix. 21.)

Sulphuret of Cyanogen.—Another sulphuret of cyanogen, different from that just described, was discovered in 1828 by M. Lassaigne. It was prepared by the action of bicyanuret of mercury in fine powder with half its weight of bichloride of sulphur, confined in a small glass globe, and exposed for two or three weeks to day-light. A small quantity of crystals, biting to the tongue and of a penetrating odour, collected in the upper part of the vessel, which formed red-coloured compounds with persalts of iron. Its constitution has not been accurately determined; and the attempts of Liebig to prepare it were unsuccessful. (An. de Ch. et de Ph. xxxix.)

Hydroseleniocyanic Acid.—The radical of this acid was obtained by Berzelius in combination with potassium, but he could not obtain the acid in a separate state. It may be regarded as a hydracid, of which seleniuret of cyanogen is the radical.

SECTION VII.

COMPOUNDS OF SULPHUR WITH CARBON, &c.

The compounds described in this section are thus constituted:

		Equiv.	Formulæ.
Bisulph. of carbon	Carb. 6.12 + Sulp. 32.2	=38.32.	$C+2S$ or CS^2.
Sulph. of phosphorus.	Composition uncertain.		
Bisulph. of selenium	Selen. 39.6 + Sulp. 32.2	=71.8.	$Se+2S$ or SeS^2.
Selen. of phosphorus.	Composition uncertain.		

Bisulphuret of Carbon.—This substance was discovered accidentally in the year 1796 by Professor Lampadius, who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius and the late Dr. Marcet. (Phil. Trans. 1813.)

Bisulphuret of carbon may be obtained by heating in close vessels native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by transmitting the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it is formed, should be conducted by means of a glass tube into cold water, at the bottom of which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with chloride of calcium.

Bisulphuret of carbon is a transparent colourless liquid, which is remarkable for its high refractive power. Its specific gravity is 1.272. It has an acid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile;—its vapour at 63.5° supports a column of mercury 7.36 inches long; and at 110° it enters into brisk ebullition. From its great volatility it may be employed for producing intense cold.

Bisulphuret of carbon is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture; and when mixed in like manner with binoxide of nitrogen, it forms a combustible mixture, which is kindled on the approach of a lighted taper, and burns rapidly, with a large greenish-white flame of dazzling brilliancy. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves sulphur, phosphorus, and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of chloride of sulphur. The pure acids have little action upon it. By nitro-hydrochloric acid it is changed into a white crystalline substance like camphor, which Berzelius regards as a compound of the hydrochloric, carbonic, and sulphurous acids.

Bisulphuret of carbon is a sulphur acid, that is, unites with *sulphur-bases* to constitute compounds analogous to ordinary salts, and hence called *sulphur-salts*. Thus bisulphuret of carbon unites with sulphuret of potassium, forming a sulphur-salt, in which the former acts as an acid and the latter as a base. The same compound is formed by the action of bisulphuret of carbon on a solution of pure potassa; but in this case sulphuret of potassium is first generated by an interchange of elements with a portion of bisulphuret of carbon, carbonic acid being produced at the same time.—Thus

2 eq. potassa & 1 eq. bisulph. carbon yield 2 eq. sulphuret potassium & 1 eq. carb. acid.

$$2(K+O) \qquad C+2S \qquad\qquad 2(K+S) \qquad C+2O.$$

If the bisulphuret of carbon is in sufficient quantity, carbonic acid gas is disengaged, and a neutral compound results. Such is inferred to be the nature of the change, agreeably to the researches of Berzelius on the sulphur-salts. The action of potassa on bisulphuret of carbon has been studied by M. Zeise, Professor of Chemistry at Copenhagen, who inferred the production of a peculiar hydracid, composed of carbon, sulphur, and hydrogen, which he thought was united with potassa; but the more probable explanation of the phenomena is that above given. (An. of Phil. xx. 241.)

Sulphuret of Phosphorus.—When sulphur and fused phosphorus are brought into contact they unite readily, but in proportions which have not been precisely determined; and they frequently react on each other with such violence as to cause an explosion. For this reason the experiment should be made with a quantity of phosphorus not exceeding 30 or 40 grains. The phosphorus is placed in a glass tube, five or six inches long, and about half an inch wide; and when by a gentle heat it is liquefied, the sulphur is added in successive small portions. Heat is evolved at the moment of combination, and hydrosulphuric and phosphoric acids, owing to the presence of moisture, are generated. This compound may also be made by agitating flowers of sulphur with fused phosphorus under water. The temperature should not exceed 160°; for otherwise hydrosulphuric and phosphoric acids would be evolved so freely as to prove dangerous, or at least to interfere with the success of the process.

Sulphuret of phosphorus, from the nature of its elements, is highly combustible. It is much more fusible than phosphorus. A compound made by Mr. Faraday with about 5 parts of sulphur and 7 of phosphorus was quite fluid at 32°, and did not solidify at 20° F. (Quarterly Journal, iv.)

Bisulphuret of Selenium.—Sulphur and selenium mix together in all proportions by fusion, and, therefore, by such means it is difficult to procure a definite compound; but the bisulphuret of an orange colour was formed by Berzelius by precipitating a solution of selenious acid with hydrosulphuric acid. The sulphuret found by Stromeyer among the volcanic products of the Lipari isles is probably similar in composition. Bisulphuret of selenium fuses at a heat a little above 212°, and at a higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids are the products of its combustion. The alkalies and soluble metallic sulphurets dissolve it. Nitric acid acts upon it with difficulty; but the nitro-hydrochloric converts it into sulphuric and selenious acids. (An. of Phil. xiv.)

Seleniuret of Phosphorus.—This compound may be prepared in the same manner as the sulphuret of phosphorus; but as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. This seleniuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus.

METALS.

GENERAL PROPERTIES OF METALS.

METALS are distinguished from other substances by the following properties. They are all conductors of electricity and heat. When the compounds which they form with oxygen, chlorine, iodine, sulphur, and similar substances, are submitted to the action of galvanism, the metals always appear at the negative side of the battery, and are hence said to be positive electrics. They are quite opaque, refusing a passage to light, though reduced to very thin leaves. They are in general good reflectors of light, and possess a peculiar lustre, which is termed the metallic lustre.—Every substance in which these characters reside may be regarded as a metal.

The number of metals, the existence of which is admitted by chemists, amounts to forty-two. The following table contains the names of those that have been procured in a state of purity, together with the date at which they were discovered, and the names of the chemists by whom the discovery was made.

Table of the Discovery of Metals.

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Gold	Known to the Ancients.	
Silver		
Iron		
Copper		
Mercury		
Lead		
Tin		
Antimony	Described by Basil Valentine	1490
Bismuth	Described by Agricola	1530
Zinc	First mentioned by Paracelsus	16th century
Arsenic	Brandt	1733
Cobalt		
Platinum	Wood, assay-master, Jamaica	1741
Nickel	Cronstedt	1751
Manganese	Gahn and Scheele	1774
Tungsten	D'Elhuyart	1781
Tellurium	Müller	1782
Molybdenum	Hielm	1782
Uranium	Klaproth	1789
Titanium	Gregor	1791
Chromium	Vauquelin	1797
Columbium	Hatchett	1802
Palladium	Wollaston	1803
Rhodium		
Iridium	Descotils and Smithson Tennant	1803
Osmium	Smithson Tennant	1803
Cerium	Hisinger and Berzelius	1804
Potassium	Davy	1807
Sodium		
Barium		
Strontium		
Calcium		
Cadmium	Stromeyer	1818
Lithium	Arfwedson	1818
Silicium	Berzelius	1824
Zirconium		
Aluminium	Wöhler	1828
Glucinium		
Yttrium		
Thorium	Berzelius	1829
Magnesium	Bussy	1829
Vanadium	Sefström	1830

Most of the metals are remarkable for their great specific gravity; some of them, such as gold and platinum, which are the densest bodies known in nature, being more than 19 times as heavy as an equal bulk of water. Great density was once supposed to be an essential characteristic of metals; but the discovery of potassium and sodium, which are so light as to float on the surface of water, has shown that this supposition is erroneous. Some metals experience an increase of density to a certain extent when hammered, their particles being permanently approximated by the operation. On this account, the density of some of the metals contained in the following table is represented as varying between two extremes.

Table of the Specific Gravity of Metals at 60° F. compared to Water as Unity.

Platinum	20.98	Brisson.
Gold	19.257	Do.
Tungsten	17.6	D'Elhuyart.
Mercury	13.568	Brisson.
Palladium	11.3 to 11.8	Wollaston.
Lead	11.352	Brisson.
Silver	10.474	Do.
Bismuth	9.822	Do.
Uranium	9.000	Buchholz.
Copper	8.895	Hatchett.
Molybdenum	8.615 to 8.636	Buchholz.
Cadmium	8.604	Stromeyer.
Cobalt	8.538	Haüy.
Nickel	8.279	Richter.
Manganese	8.013	John.
Iron	7.788	Brisson.
Tin	7.291	Do.
Zinc	6.861 to 7.1	Do.
Antimony	6.702	Do.
Tellurium	6.115	Klaproth.
Arsenic	5.8843	Turner.
Titanium	5.3	Wollaston.
Sodium	0.972	Gay-Lussac and Thenard.
Potassium	0.865	

Some metals possess the property of *malleability*, that is, admit of being beaten into thin plates or leaves by hammering. The malleable metals are gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and frozen mercury. The other metals are either malleable in a very small degree only, or, like antimony, arsenic, and bismuth, are actually brittle. Gold surpasses all metals in malleability: one grain of it may be extended so as to cover about 52 square inches of surface. and to have a thickness not exceeding $\frac{1}{282020}$th of an inch.

Nearly all malleable metals may be drawn out into wires, a property which is expressed by the term *ductility*. The only metals which are remarkable in this respect are gold, silver, platinum, iron, and copper. Wollaston devised a method by which gold wire may be obtained so fine that its diameter shall be only $\frac{1}{5000}$th of an inch, and that 550 feet of it are required to weigh one grain. He obtained a platinum wire so small, that its diameter did not exceed $\frac{1}{30000}$th of an inch. (Philos. Trans. 1813.) It is singular that the ductility and malleability of the same metal are not always in proportion to each other. Iron, for example, cannot be made into fine leaves, but it may be drawn into very small wires.

The tenacity of metals is measured by ascertaining the greatest weight which a wire of a certain thickness can support without breaking. According to the experiments of Guyton-Morveau, whose results are comprised in the following table, iron, in point of tenacity, surpasses all other metals.

The diameter of each wire was 0.787th of a line.

	Pounds.
Iron wire supports	549.25
Copper	302.278
Platinum	274.32
Silver	187.137
Gold	150.753
Zinc	109.54
Tin	34.63
Lead	27.621

Metals differ also in hardness, but I am not aware that their exact relation to each other, under this point of view, has been determined by experiment. In the list of hard metals may be placed titanium, manganese, iron, nickel, copper, zinc, and palladium. Gold, silver, and platinum, are softer than these; lead is softer still, and potassium and sodium yield to the pressure of the fingers. The properties of elasticity and sonorousness are allied to that of hardness. Iron and copper are in these respects the most conspicuous.

Many of the metals have a distinctly crystalline texture. Iron, for example, is fibrous; and zinc, bismuth and antimony are lamellated. Metals are sometimes obtained also in crystals; and most of them in crystallizing, assume the figure of a cube, the regular octohedron, or some form allied to it. Gold, silver, and copper, occur naturally in crystals, while others crystallize when they pass gradually from the liquid to the solid condition. Crystals are most readily procured from those metals which fuse at a low temperature; and bismuth, from conducting heat less perfectly than other metals, and, therefore, cooling more slowly, is best fitted for the purpose. The process should be conducted in the way already described for forming crystals of sulphur. (Page 191.)

Metals, with the exception of mercury, are solid at common temperatures; but they may all be liquefied by heat. The degree at which they *fuse*, or their *point* of *fusion*, is very different for different metals, as appears from the following table.

Table of the Fusibility of different Metals.

			Fahr.	
Fusible below a red heat.	Mercury		—39°	Different chemists.
	Potassium		136	Gay-Lussac and Thenard.
	Sodium		190	
	Cadmium	about	442	Stromeyer.
	Tin		442	Crichton.
	Bismuth		497	
	Lead		612	
	Tellurium—rather less fusible than lead.			Klaproth.
	Arsenic—undetermined.			
	Zinc		773	Daniell.
	Antimony—a little below a red heat.			
Infusible below a red heat.	Silver		1873	Daniell.
	Copper		1996	
	Gold		2016	
	Iron, cast		2786	
	Iron, malleable			Requiring the highest heat of a smith's forge.
	Manganese			
	Cobalt—rather less fusible than iron.			
	Nickel—nearly the same as cobalt.			
	Palladium			

Infusible below a red heat.	Molybdenum Uranium Tungsten Chromium	Almost infusible, and not to be procured in buttons by the heat of a smith's forge.	Fusible before the oxy-hydrogen blowpipe.
	Titanium Cerium Osmium Iridium Rhodium Platinum Columbium	Infusible in the heat of a smith's forge, but fusible before the oxy-hydrogen blowpipe.	

Metals differ also in volatility. Some are readily volatilized by heat, while others are of so fixed a nature that they may be exposed to the most intense heat of a wind furnace without being dissipated in vapour. There are seven metals, the volatility of which has been ascertained with certainty; namely, cadmium, mercury, arsenic, tellurium, potassium, sodium, and zinc.

Metals cannot be resolved into more simple parts; and, therefore, in the present state of chemistry, they must be regarded as elementary bodies. It was formerly conceived that they might be converted into each other; and this notion led to the vain attempts of the alchemists to convert the baser metals into gold. The chemist has now learned that his art solely consists in resolving compound bodies into their elements, and causing substances to unite which were previously uncombined. One elementary principle cannot assume the properties peculiar to another.

Metals have an extensive range of affinity. and on this account few of them are found in the earth *native*, that is, in an uncombined form. They commonly occur in combination with other bodies, especially with oxygen and sulphur, in which state they are said to be *mineralized*. It is a singular fact in the chemical history of the metals, that they are little disposed to combine in the metallic state with compound bodies, such as an oxide or an acid. They unite readily, on the contrary, with elementary substances. Thus, they often combine with each other, yielding compounds termed *alloys*, which possess all the characteristic physical properties of pure metals. They unite likewise with the simple substances not metallic, such as oxygen, chlorine, and sulphur, giving rise to new bodies in which the metallic character is wholly wanting. In all these combinations, the same tendency to unite in a few definite proportions is equally conspicuous as in that department of the science of which I have just completed the description. The chemical changes are regulated by the same general laws, and in describing them the same nomenclature is applicable.

The order which it is proposed to follow in describing the metals has already been explained in the introduction; but before treating of each separately, some general observations may be premised, by which the study of this subject will be much facilitated.

Metals are of a combustible nature; that is, they are not only susceptible of slow oxidation, but, under favourable circumstances, they unite rapidly with oxygen, giving rise to all the phenomena of real combustion. Zinc burns with a brilliant flame when heated to full redness in the open air; iron emits vivid scintillations on being inflamed in an atmosphere of oxygen gas; and the least oxidable metals, such as gold and platinum, scintillate in a similar manner when heated by the oxy-hydrogen blowpipe.

The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration;* that is, by mixing them with nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitrohydrochloric acid is an oxidizing agent of still greater power.

Some metals unite with oxygen in one proportion only, but most of them have two or three degrees of oxidation. Metals differ remarkably in their relative forces of attraction for oxygen. Potassium and sodium, for example, are oxidized by mere exposure to the air; and they decompose water at all temperatures, the instant they come in contact with it. Iron and copper may be preserved in dry air without change, nor can they decompose water at common temperatures; but they are both slowly oxidized by exposure to a moist atmosphere, and combine rapidly with oxygen when heated to redness in the open air. Iron has a stronger affinity for oxygen than copper; for the former decomposes water at a red heat, whereas the latter cannot produce that effect. Mercury is less inclined than copper to unite with oxygen. Thus it may be exposed without change to the influence of a moist atmosphere. At a temperature of 650° or 700° it is oxidized; but at a red heat it is reduced to the metallic state, while oxide of copper can sustain the strongest heat of a blast furnace without losing its oxygen. The affinity of gold for oxygen is still weaker than that of mercury; for it will bear the most intense heat of our furnaces without oxidation.

Metallic oxides suffer *reduction*, or may be reduced to the metallic state in several ways:

1. By heat alone. By this method the oxides of gold, silver, mercury, and platinum may be decomposed.

2. By the united agency of heat and combustible matter. Thus, by transmitting a current of hydrogen gas over the oxides of copper or iron heated to redness in a tube of porcelain, water is generated, and the metals are obtained in a pure form. Carbonaceous matters are likewise used for the purpose with great success. Potassa and soda, for example, may be decomposed by exposing them to a white heat after being intimately mixed with charcoal in fine powder. A similar process is employed in metallurgy for extracting metals from their ores, the inflammable materials being wood, charcoal, coke, or coal. In the more delicate operations of the laboratory, charcoal and *black flux* are preferred.

3. By the galvanic battery. This is a still more powerful agent than the preceding; since some oxides, such as baryta and strontia, which resist the united influence of heat and charcoal, are reduced by the agency of galvanism.

4. By the action of deoxidizing agents on metallic solutions. Phosphorous acid, for example, when added to a liquid containing oxide of mercury, deprives the oxide of its oxygen, metallic mercury subsides, and phosphoric acid is generated. In like manner, one metal may be precipitated by another, provided the affinity of the latter for oxygen exceeds that of the former. Thus, when mercury is added to a solution of nitrate of the oxide of silver, metallic silver is thrown down, and oxide of mercury is dissolved by the nitric acid. On placing metallic copper in the liquid, pure mercury subsides, and a nitrate of the oxide of copper is formed; and from this solution metallic copper may be precipitated by means of iron.

Metals, like the simple non-metallic bodies, may give rise to oxides or acids by combining with oxygen. The former are the most frequent products. Many metals which are not acidified by oxygen may be formed into oxides; whereas one metal only, arsenic, is capable of forming an acid and not an oxide. All the other metals which are convertible into acids by oxygen, such as chromium, tungsten, and molybdenum, are also susceptible of yielding one or more oxides. In these instances, the acids always contain a larger quantity of oxygen than the oxides of the same metal.

Many of the metallic oxides have the property of combining with acids. In some instances all the oxides of a metal are capable of forming salts with acids, as is exemplified by the oxides of iron; but, generally, the protoxide is the sole *alkaline* or *salifiable base*. Most of the metallic oxides are insoluble in water; but all those that are soluble have the property of giving a brown stain to yellow turmeric paper, and of restoring the blue colour of reddened litmus.

Oxides sometimes unite with each other, and form definite compounds. The most abundant ore of chromium, commonly called chromate of iron, is an instance of this kind; and the red and sesquioxide of manganese, and the red oxide of lead appear to belong to the same class of bodies.

Chlorine has a powerful affinity for metallic substances. It combines readily with most metals at common temperatures, and the action is in many instances so violent as to be accompanied with the evolution of light. For example, when powdered zinc, arsenic, or antimony is thrown into a jar of chlorine gas, the metal is instantly inflamed. The attraction of chlorine for metals even surpasses that of oxygen. Thus, when chlorine is brought into contact at a red heat with pure lime, magnesia, baryta, strontia, potassa, or soda, oxygen is emitted, and a chloride of the metal is generated, the elements of which are so strongly united that no temperature hitherto tried can separate them. All other metallic oxides are, with few exceptions, acted on in the same manner by chlorine, and in some cases the change takes place below the temperature of ignition.

Most of the metallic chlorides are solid at common temperatures. They are fusible by heat, assume a crystalline texture in cooling, and under favourable circumstances crystallize with regularity. Several of them, such as the chlorides of tin, arsenic, antimony, and mercury, are volatile, and may be sublimed without change. They are for the most part colourless, do not possess the metallic lustre, and have the aspect of a salt. Two of the chlorides are insoluble in water, namely, chloride of silver and protochloride of mercury; several, such as the chlorides of antimony, arsenic, and titanium, are decomposed by that liquid; but most of them are more or less soluble.

Some of the metallic chlorides, those especially of gold and platinum, are decomposable by heat. All the chlorides of the common metals are decomposed at a red heat by hydrogen gas, hydrochloric acid being disengaged while the metal is set free. Pure charcoal does not effect their decomposition; but if moisture be present at the same time, hydrochloric and carbonic acid gases are formed, and the metal remains. They resist the action of anhydrous sulphuric acid; but all the chlorides, excepting those of silver and mercury, are readily decomposed by hydrated sulphuric acid, with disengagement of hydrochloric acid gas. The change is accompanied with decomposition of water, the hydrogen of which combines with chlorine, and its oxygen with the metal. All chlorides, when in solution, may be recognized by yielding, with nitrate of oxide of silver, a white precipitate, which is chloride of silver.

Metallic chlorides may in most cases be formed by direct action of chlorine on the pure metals. They are also frequently procured by dissolving metallic oxides in hydrochloric acid, evaporating to dryness, and applying heat so long as any water is expelled. Metallic chlorides are often deposited from such solutions by crystallization.

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As fluorine has not hitherto been obtained in a separate state, the nature of its action on the metals is unknown; but the chief difficulty of procuring it in an insulated form appears to arise from its extremely powerful affinity for metallic substances, in consequence of which, at the moment of becoming free, it attacks the vessels and instruments employed in its preparation. The best mode of preparing the soluble fluorides, such as those of potassium and sodium, is by dissolving the carbonate of these alkalies in hydrofluoric acid, and evaporating the solution to perfect dryness. The insoluble fluorides are easily formed by precipitation from the soluble fluorides. They are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydrofluoric acid, in escaping, may easily be detected by its action on glass.

Sulphur, like the preceding elementary substances, has a strong tendency to unite with metals, and the combination may be effected in several ways:

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of sulphur, and the mixture heated in an earthen crucible, which is covered to prevent the access of air; or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by free disengagement of heat, which in several instances is so great, that the whole mass becomes luminous, and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.

2. By igniting a mixture of a metallic oxide and sulphur.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By hydrosulphuric acid, or a soluble metallic sulphuret. Nearly all the salts of the second class of metals are decomposed when a current of hydrosulphuric acid gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel are exceptions; but these are precipitated by sulphuret of potassium.

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Most of the protosulphurets support an intense heat without decomposition; but, in general, those which contain more than one equivalent of sulphur, lose part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of air or oxygen gas and heat; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is more or less converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, the sulphur is evolved under the form of sulphurous acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes. A few sulphurets are decomposed by the action of hydrogen gas at a red heat, the pure metal being set free and hydrosulphuric acid evolved. Rose finds that the only sulphurets which admit of being easily reduced to the metallic state in this way are those of antimony, bismuth, and silver. The sulphuret of tin is decomposed with difficulty, and requires a very high temperature. All the other sulphurets which he subjected to this treatment were either deprived of a part only of their sulphur, such as bisulphuret of iron, or were not attacked at all, as happened with the sulphurets of zinc, lead, and copper. (Poggendorff's Annalen, iv. 109.)

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Berzelius has published some ingenious remarks in order to prove that chlorine does not unite with metallic oxides, and that the bleaching compounds, supposed to be examples of such a mode of combination, are mixtures of a metallic chloride and a *chlorite* of an oxide. The supposed chlorite, when heated, passes into a chlorate and chloride; but if colouring matter or an oxidable substance be present, the chlorous acid yields its oxygen, and a metallic chloride results. The bleaching power of the compound is of course attributed to the oxygen which is set at liberty. This point is powerfully argued by Berzelius, and supported on well-contrived experiments; but since no decisive proof of the existence of such a compound as chlorous acid has as yet been given, there appears to be no sufficient reason for rejecting the explanation generally adopted by chemists. (An. de Ch. et de Ph. xxxviii. 208.)

Iodine has a strong attraction for metals; and most of the compounds which it forms with them sustain a red heat in close vessels without decomposition. But in the degree of its affinity for metallic substances it is inferior to chlorine and oxygen. We have seen that chlorine has a stronger affinity than oxygen for metals, since it decomposes nearly all oxides at high temperatures; and it separates iodine also from metals under the same circumstances. If the vapour of iodine is brought into contact with potassa, soda, protoxide of lead, or oxide of bismuth, heated to redness, oxygen gas is evolved, and the metals of those oxides will unite with iodine. But iodine, so far as is known, cannot separate oxygen from any other metal; nay, all the iodides, except those just mentioned, are decomposed by exposure to oxygen gas at the temperature of ignition. All the iodides are decomposed by chlorine, bromine, and concentrated sulphuric and nitric acids; and the iodine which is set free may be recognized either by the colour of its vapour, or by its action on starch. (Page 227.) The metallic iodides are generated under circumstances analogous to those above mentioned for procuring the chlorides.

When the vapour of iodine is conducted over red-hot lime, baryta, or strontia, oxygen is not disengaged, but an iodide of those oxides, according to Gay-Lussac, is generated. The iodides of these oxides are, therefore, more permanent than the analogous compounds with chlorine. Iodine does not combine with any other oxide under the same circumstances; and indeed all other such iodides, very few of which exist, are, like the chlorides of oxides, possessed of little permanency, and are decomposed by a red heat.

The action of iodine on metallic oxides, when dissolved or suspended in water, is precisely analogous to that of chlorine. On adding iodine to a solution of the pure alkalies or alkaline earths, an iodide and iodate are generated.

Bromine, in its affinity for metallic substances, is intermediate between chlorine and iodine; for while chlorine disengages bromine from its combination with metals, metallic iodides are decomposed by bromine. The same phenomena attend the union of bromine with metals, as accompany the formation of metallic chlorides. Thus, antimony and tin take fire by contact with bromine, and its action with potassium is attended with a flash of light and intense heat. These compounds have as yet been but partially examined. They may be formed by the action of bromine on the pure metals, and often by dissolving metallic oxides in hydrobromic acid, and evaporating the solution to dryness. Bromine unites with potassa, soda, and some other oxides, constituting bleaching compounds similar to the chlorides above described. Bromide of lime is obtained by the action of bromine on milk of lime, a yellowish solution being formed with water, which bleaches powerfully.

As fluorine has not hitherto been obtained in a separate state, the nature of its action on the metals is unknown; but the chief difficulty of procuring it in an insulated form appears to arise from its extremely powerful affinity for metallic substances, in consequence of which, at the moment of becoming free, it attacks the vessels and instruments employed in its preparation. The best mode of preparing the soluble fluorides, such as those of potassium and sodium, is by dissolving the carbonate of these alkalies in hydrofluoric acid, and evaporating the solution to perfect dryness. The insoluble fluorides are easily formed by precipitation from the soluble fluorides. They are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydrofluoric acid, in escaping, may easily be detected by its action on glass.

Sulphur, like the preceding elementary substances, has a strong tendency to unite with metals, and the combination may be effected in several ways:

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of sulphur, and the mixture heated in an earthen crucible, which is covered to prevent the access of air; or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by free disengagement of heat, which in several instances is so great, that the whole mass becomes luminous, and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.

2. By igniting a mixture of a metallic oxide and sulphur.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By hydrosulphuric acid, or a soluble metallic sulphuret. Nearly all the salts of the second class of metals are decomposed when a current of hydrosulphuric acid gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel are exceptions; but these are precipitated by sulphuret of potassium.

The sulphurets are opaque brittle solids, many of which, such as the sulphurets of lead, antimony, and iron, have a metallic lustre. They are all fusible by heat, and commonly assume a crystalline texture in cooling. Most of them are fixed in the fire; but the sulphurets of mercury and arsenic are remarkable for their volatility. All the sulphurets, excepting those of the first class of metals, are insoluble in water.

Most of the protosulphurets support an intense heat without decomposition; but, in general, those which contain more than one equivalent of sulphur, lose part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of air or oxygen gas and heat; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is more or less converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, the sulphur is evolved under the form of sulphurous acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes. A few sulphurets are decomposed by the action of hydrogen gas at a red heat, the pure metal being set free and hydrosulphuric acid evolved. Rose finds that the only sulphurets which admit of being easily reduced to the metallic state in this way are those of antimony, bismuth, and silver. The sulphuret of tin is decomposed with difficulty, and requires a very high temperature. All the other sulphurets which he subjected to this treatment were either deprived of a part only of their sulphur, such as bisulphuret of iron, or were not attacked at all, as happened with the sulphurets of zinc, lead, and copper. (Poggendorff's Annalen, iv. 109.)

Many of the metallic sulphurets were formerly thought to be compounds of sulphur and a metallic oxide; an error first pointed out by Proust, who demonstrated that protosulphuret of iron, as well as the bisulphuret, are compounds of sulphur and metallic iron without any oxygen. (Journal de Physique, liii.) He proved the same of the sulphurets of other metals, such as mercury and copper. He was of opinion, however, that in some instances sulphur does unite with a metallic oxide. Thus, when sulphur and peroxide of tin are heated together, sulphurous acid is disengaged, and the residue, according to Proust, is a sulphuret of the protoxide, but in this he was in error.

In 1817 Vauquelin extended these views to the compounds formed by heating an alkali or an alkaline earth with sulphur, which were previously regarded as sulphurets of a metallic oxide. He explained that the elements of the alkali unite with separate portions of sulphur, forming a metallic sulphuret and sulphuric acid, the latter of which unites with undecomposed alkali. Thus, in preparing the so-called *liver of sulphur*, made by fusing carbonate of potassa with sulphur, one portion of the alkali is completely decomposed, its elements unite separately with sulphur, giving rise to sulphuret of potassium and sulphuric acid, the latter of which combines with undecomposed potassa. These views were at the same time supported by Gay-Lussac. (An. de Ch. et de Ph. vi.)

One of the chief arguments adduced by Vauquelin in support of his opinion was drawn from the action of charcoal on sulphate of potassa. When a mixture of this salt with powdered charcoal is ignited without exposure to the air, carbonic oxide and carbonic acid gases are formed, and a sulphuret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potassa directly with sulphur. They are both essentially the same substance, and Vauquelin conceived from the strong attraction of carbon for oxygen, that both the sulphuric acid and potassa would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

Berthier has proved that these changes do actually occur. (An. de Ch. et de Ph. xxii.) He put a known weight of sulphate of baryta into a crucible lined with a mixture of clay and charcoal, defended it from contact with the air, and exposed it to a white heat for the space of two hours. By this treatment it suffered complete decomposition, and it was found that in passing into a sulphuret, it had suffered a loss in weight precisely equal to the quantity of oxygen originally contained in the acid and earth. This circumstance, coupled with the fact that there had been no loss of sulphur, is decisive evidence that the baryta as well as the acid had lost its oxygen, and that a sulphuret of barium had been formed. He obtained the same results also with the sulphates of strontia, lime, potassa, and soda; but from the light fusibility of the sulphurets of potassium and sodium, their loss of weight could not be determined with such precision as in the other instances.

The experiments of Berzelius, performed about the same time, are exceedingly elegant, and still more satisfactory than the foregoing. (An. de Ch. et de Ph. xx.) He transmitted a current of dry hydrogen gas over a known quantity of sulphate of potassa, heated to redness. It was expected from the strong affinity of hydrogen for oxygen, that the sulphate would be decomposed; and, accordingly, a considerable quantity of water was formed, which was carefully collected and weighed. The loss of weight which the salt had experienced was precisely equivalent to the oxygen of the acid and alkali; and the oxygen of the water was exactly equal to the loss in weight. A similar result was obtained with the sulphates of soda, baryta, strontia, and lime.

It is demonstrated, therefore, that the metallic bases of the alkalies and alkaline earths agree with the common metals in their disposition to unite with sulphur. It is now certain that, whether a sulphate be decomposed by hydrogen or charcoal, or sulphur ignited with an alkali or alkaline earth, a metallic sulphuret is always the product. Direct combination between sulphur and a metallic oxide is a very rare occurrence, nor has the existence of such a compound been clearly established. Gay-Lussac indeed states that, when an alkali or an alkaline earth is heated with sulphur in such a manner that the temperature is never so high as a low red heat, the product is really the sulphuret of an oxide. But the facts adduced in favour of this opinion are not altogether satisfactory, so that the real nature of the product must be decided by future observation.

Several of the metallic sulphurets occur abundantly in nature. Those that are most frequently met with are the sulphurets of lead, antimony, copper, iron, zinc, molybdenum, and silver.

The metallic seleniurets have so close a resemblance in their chemical relations to the sulphurets, that it is unnecessary to give a separate description of them. They may be prepared either by bringing selenium in contact with the metals at a high temperature, or by the action of hydroselenic acid on metallic solutions.

Cyanogen, as mentioned at page 265, has an affinity for metallic substances. Nearly all the cyanurets of the second class of metals are insoluble in water, and may be obtained by precipitation with cyanuret of potassium. Most of them are decomposed by a red heat even without exposure to the air.

Cyanogen unites also with some of the metallic oxides. When hydrocyanic acid vapour is transmitted over pure baryta contained in a porcelain tube, and heated till it begins to be luminous, hydrogen gas is evolved, and cyanuret of baryta, according to Gay-Lussac, is generated. The same chemist succeeded in forming the cyanurets of potassa and soda by a similar process. These compounds exist only in the dry state. A change is produced in them by the action of water, the nature of which has already been explained. (Page 270.)

Respecting the preceding compounds there remains one subject, the consideration of which, as applying equally to all, has been purposely delayed. The non-metallic ingredient of each of these compounds is the radical of a hydracid; that is, has the property of forming with hydrogen an acid, which, like other acids, is unable to unite with metals, but appears to combine readily with many metallic oxides. Owing to this circumstance, a difficulty arises in explaining the action of such substances on water. Thus, when chloride of potassium is put into water, it may dissolve without suffering any other chemical change, and the liquid accordingly contain chloride of potassium in solution. But it is also possible that the elements of this compound may react on those of water, its potassium uniting with oxygen, and its chlorine with hydrogen; and as the resulting potassa and hydrochloric acid have a strong affinity for each other, the solution would of course contain hydrochlorate of potassa. A similar uncertainty attends the action of water on other metallic chlorides, and on the compounds of metals with iodine, bromine, sulphur, and similar substances; so that when iodide, sulphuret, and cyanuret of potassium are put into water, it may be doubted whether they dissolve as such, or whether they may not be converted, by decomposition of water, into hydriodate, hydrosulphate, and hydrocyanate of potassa. This question would at once be decided, could it be ascertained whether water is or is not decomposed during the process of solution; but this is the precise point of difficulty, since, from the operation of the laws of chemical union, no disengagement of gas does or can take place, by which the occurrence of such a change may be indicated. Chemists, accordingly, being guided by probabilities, are divided in opinion, and I shall, therefore, give a brief statement of both views, with the arguments in favour of each.

According to one view, then, chloride of potassium and all similar compounds dissolve in water without undergoing any other change, and are deposited in their original state by crystallization. When any hydracid, such as hydrochloric or hydriodic acid, is mixed with potassa or any similar metallic oxide, the acid and salifiable base do not unite; but the oxygen of the oxide combines with the hydrogen of the acid, and the metal itself with the radical of the hydracid. This kind of double decomposition unquestionably takes place in some instances, as when hydrosulphuric acid acts upon acetate of oxide of lead, the insoluble sulphuret of lead being actually precipitated; but it is also thought to occur even when the transparency of the solution is undisturbed. It is argued, accordingly, that hydrochlorate of potassa, and the salts of the hydracids in general have no existence. Thus, when nitrate of the oxide of silver is added to a solution of chloride or cyanuret of potassium, metallic silver is said to unite with chlorine or cyanogen, while the oxygen of the oxide of silver combines with potassium; so that nitrate of potassa and chloride or cyanuret of silver are generated. On adding sulphuric acid to a solution of chloride of potassium, hydrochloric acid and potassa, which did not previously exist, are instantly formed in consequence of water being decomposed, and yielding its hydrogen to chlorine, and its oxygen to potassium; exactly as happens when concentrated sulphuric acid is brought into contact with solid chloride of potassium. It is further believed that the crystallized hydrochlorate of lime, baryta, and strontia, which contain water or its elements, are metallic chlorides combined with water of crystallization; and the same view is applied to all analogous compounds.

According to the other doctrine, chloride of potassium is converted into hydrochlorate of potassa in the act of dissolving; and when the solution is evaporated, the elements existing in the salt reunite at the moment of crystallization, and crystals of chloride of potassium are deposited. The same explanation applies in all cases, when the salt of a hydracid crystallizes without retaining the elements of water. Of those compounds which in crystallizing retain water or its elements in combination, two opinions may be formed. Thus crystallized hydrochlorate of baryta, which consists of one equivalent of chlorine, one of barium, two of oxygen, and two of hydrogen, may be regarded as a compound either of hydrochlorate of baryta with one equivalent of water of crystallization, or of chloride of barium with two equivalents of water. When exposed to heat, two equivalents of water are expelled, and chloride of barium is left. When nitrate of the oxide of silver is mixed in solution with hydrochlorate of potassa, the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, chloride of silver is precipitated, and nitrate of potassa remains in the liquid. On adding sulphuric acid to a hydrochlorate, hydrochloric acid is simply displaced, just as when carbonic acid in marble is separated from lime by the action of nitric acid.

On comparing these opinions it is manifest that both are consistent with well-known affinities. When a metallic chloride is dissolved in water, the attraction of chlorine for the metal, and that of oxygen for hydrogen, tend to prevent chemical change; but the affinities of the metal for oxygen, of chlorine for hydrogen, and of hydrochloric acid for metallic oxides, co-operate in determining the decomposition of water, and the production of a hydrochlorate. In favour of the latter view, the following considerations may be adduced:—1. The solution of some compounds, such as sulphuret and cyanuret of potassium, actually emit an odour of hydrosulphuric and hydrocyanic acid. 2. Other compounds, such as the chlorides of copper, cobalt, and nickel, instantly acquire, when put into water, the colour peculiar to the salts of the oxides of those metals. 3. The solution of protochloride of iron, like the protosulphate, absorbs oxygen from the atmosphere; an effect which seems to indicate the presence of the protoxide of iron in the liquid. 4. In some instances there is direct proof of decomposition of water. Thus when sulphuret of aluminium is put into that fluid, alumina is generated, and hydrosulphuric acid gas disengaged with effervescence. In like manner chloride and sulphuret of silicium are converted by water into silica, and hydrochloric and hydrosulphuric acid. In these cases the want of affinity between the new compounds causes their separation, and thus affords direct proof that water is decomposed. But the affinities which produce this change do not appear so likely to be effective, as those which are in operation when chloride of potassium is put into water; especially when it is considered that the attraction of chlorine for hydrogen, and potassium for oxygen, is aided by that of the resulting acid and oxide for each other.

These arguments may be successively answered in the following manner:—1. That solutions of cyanuret and sulphuret of potassium smell of hydrocyanic and hydrosulphuric acids, because the carbonic acid of the atmosphere gradually decomposes them. 2. That metals may yield with chlorine compounds of the same colour as the oxides of the same metals. Thus the terchloride and terfluoride of chromium have a red colour closely resembling that of chromic acid. 3. Protochloride of iron may attract oxygen from the air because of its known tendency to pass into the state of a sesquichloride, a portion of iron being at the same time converted into peroxide. 4. That while certain chlorides do really decompose water, it must be conceded that others dissolve directly without change. The bichloride of platinum and terchloride of gold are soluble in ether, forming solutions which must be regarded as chlorides and not hydrochlorates, since pure ether is anhydrous; and when aqueous solutions of these chlorides are agitated with ether, ethereal solutions of platinum and gold are formed, exactly similar to those made with ether alone. It can scarcely be doubted, then, that these chlorides exist as such in water. In favour of the same view it may with truth be alleged, that the chlorides of potassium and sodium dissolve in and crystallize out of water without evincing the least sign of any other change than mere solution and mere crystallization. Again, crystals of the so-called hydrochlorate of baryta become chloride of barium with loss of water by mere exposure to a dry air; a cause apparently inadequate to determine the hydrogen of the acid to unite with the oxygen of the oxide, but sufficient to explain the phenomena if the crystals were chloride of barium with water of crystallization.

On weighing these and other considerations of a like kind, it appears undeniable that *some* metallic chlorides, iodides, cyanurets, and similar compounds dissolve as such in water; that all do so, is a position which cannot, I think, be maintained; and, therefore, the existence of such compounds as hydracids united with metallic oxides can scarcely be denied. At the same time it is necessary, to avoid a perpetually recurring two-fold explanation, to adhere consistently to one view; and the reader may have observed that I have, in this edition, uniformly gone on the supposition that chlorides, and the same class of bodies, dissolve as such in water. The considerations which have led to this preference are principally drawn from the history of the sulphur-salts.

Chemists are acquainted with several metallic phosphurets; and it is probable that phosphorus, like sulphur, is capable of uniting with all the metals. Little attention, however, has hitherto been devoted to these compounds; and for the greater part of our knowledge concerning them we are indebted to the researches of Pelletier and Rose. (An. de Ch. i. and xiii.; and Pog. Annalen, vi. 205.)

The metallic phosphurets may be prepared in several ways. The mos direct method is by bringing phosphorus in contact with metals at a high temperature, or by igniting metals in contact with phosphoric acid and charcoal. Several of the phosphurets may be formed by transmitting a current of phosphuretted hydrogen gas over metallic oxides heated to redness in a porcelain tube, when water is generated, and a phosphuret of the metal remains. By similar treatment the chlorides and sulphurets of many metals may be decomposed, and phosphurets formed, provided the metal is capable of retaining phosphorus at a red heat. According to Rose, the phosphurets of copper, nickel, cobalt, and iron are the only ones which admit of being advantageously prepared by this method. When chlorides are employed, hydrochloric acid, and with sulphurets hydrosulphuric acid gas, is of course generated.

Phosphorus is said to unite with metallic oxides. For example, phosphuret of lime is said to be formed by conducting the vapour of phosphorus over that earth at a low red heat; but it is probable that in this instance, as with a mixture of sulphur and an alkali, part of the metallic oxide is decomposed, and that the product contains phosphuret of calcium and phosphate of lime.

The only metallic carburets of importance are those of iron, which will be described in the section on that metal.

Hydrogen unites with few metals. The only metallic hydroguretѕ, or hydurets known are those of zinc, potassium, arsenic, and tellurium. No definite compound of nitrogen and a metal has hitherto been discovered.

The discoveries of modern chemistry have materially added to the number of the metals, especially by associating with them a class of bodies which was formerly believed to be of a nature entirely different. The metallic bases of the alkalies and earths, previous to the year 1807, were altogether unknown; and before that date the list of metals, with few exceptions, included those only which are commonly employed in the arts, and which are hence often called the common metals. In consequence of this increase in number, it is found convenient, for the purpose of description, to arrange them in separate groups; and as the alkalies and earths differ in several respects from the oxides of other metals, it will be convenient to describe them separately. I have accordingly divided the metals into the two following classes:—

Class I. Metals which by oxidation yield alkalies or earths.

Class II. Metals, the oxides of which are neither alkalies nor earths.

Class I. This class includes thirteen metals, which may properly be arranged in three orders.

Order 1. Metallic bases of the alkalies. They are three in number; namely,

Potassium, Sodium, Lithium.

These metals have such a powerful attraction for oxygen, that they decompose cold water and even ice at the moment of contact, and are oxidized with disengagement of hydrogen gas. The resulting oxides are distinguished by their causticity and solubility in water, and by possessing alkaline properties in an eminent degree. They are called *alkalies*, and their metallic bases are sometimes termed *alkaline* or *alkaligenous* metals.

Order 2. Metallic bases of the alkaline earths. These are four in number; namely,

Barium, Strontium, Calcium, Magnesium.

These metals, excepting magnesium, also decompose water rapidly at common temperatures. The resulting oxides are called *alkaline earths;* because, while in their appearance they resemble the earths, they are similar to the alkalies in having a strong alkaline reaction with test paper, and in neutralizing acids. The three first are strongly caustic, and baryta and strontia are soluble in water to a considerable extent.

Order 3. Metallic bases of the earths. These are six in number; namely,

Aluminium, Yttrium, Zirconium,
Glucinium, Thorium, Silicium.

The oxides of these metals are well known as the pure earths. They are white and of an earthy appearance, in their ordinary state are quite insoluble in water, and do not affect the colour of turmeric or litmus paper. As salifiable bases they are inferior to the alkaline earths. Silica is even considered by several chemists as an acid, and its chemical relations appear to justify the opinion. For reasons to be afterwards mentioned, the propriety of placing silicium among the metals is exceedingly doubtful.

Class II. The number of the metals included in this class amounts to twenty-nine. They are all capable of uniting with oxygen, and generally in more than one proportion. Their protoxides have an earthy appearance, but with few exceptions are coloured. They are insoluble in water, and in general do not affect the colour of test paper. Most of them act as salifiable bases in uniting with acids, and forming salts; but in this respect they are much inferior to the alkalies and alkaline earths, by which they may be separated from their combinations. Several of these metals are capable of forming with oxygen compounds, which possess the character of acids. The metals in which this property has been noticed are manganese, arsenic, chromium, vanadium, molybdenum, tungsten, columbium, antimony, titanium, tellurium, and gold.

The metals belonging to the second class may be conveniently arranged in the three following orders:—

Order 1. Metals which decompose water at a red heat. They are seven in number; namely,

Manganese,
Iron,
Zinc,
Cadmium,
Tin,
Cobalt,
Nickel.

Order 2. Metals which do not decompose water at any temperature, and the oxides of which are not reduced to the metallic state by the sole action of heat. Of these there are fourteen in number; namely,

Arsenic,
Chromium,
Vanadium,
Molybdenum,
Tungsten,
Columbium,
Antimony,
Uranium,
Cerium,
Bismuth,
Titanium,
Tellurium,
Copper,
Lead.

Order 3. Metals, the oxides of which are decomposed by a red heat. These are

Mercury,
Silver,
Gold,
Platinum,
Palladium,
Rhodium,
Osmium,
Iridium.

CLASS I.

METALS WHICH BY OXIDATION YIELD ALKALIES OR EARTHS.

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

Potassium, or kalium, was discovered in the year 1807 by Sir H. Davy, and the circumstances which led to the discovery have already been described. Hydrate of potassa, slightly moistened for the purpose of increasing its conducting power, was made to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potassa passed over to the positive pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative pole. By this process potassium is obtained in small quantity only; but Gay-Lussac and Thenard invented a method by which a more abundant supply may be procured. (Recherches Physico-Chimiques, vol. i.) Their process consists in bringing fused hydrate of potassa in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potassa of oxygen, hydrogen gas combined with a little potassium is evolved, and pure potassium sublimes, and may be collected in a cool part of the apparatus.

Potassium may also be prepared, as first noticed by M. Curaudau, by mixing dry carbonate of potassa with half its weight of powdered charcoal, and exposing the mixture, contained in a gun-barrel or spheroidal iron bottle, to a strong heat. An improvement on both processes has been made by M. Brunner, who decomposes potassa by means of iron and charcoal. From eight ounces of fused carbonate of potassa, six ounces of iron filings, and two ounces of charcoal mixed intimately and heated in an iron bottle, he obtained 140 grains of potassium. (Quarterly Journal, xv. 379.) Berzelius has observed that the potassium thus made, though fit for all the usual purposes to which it is applied, contains a minute quantity of carbon; and, therefore, if required to be quite pure, must be rendered so by distillation in a retort of iron or green glass. A modification of this process has been since described by Wöhler, who effects the decomposition of the potassa solely by means of charcoal. The material employed for the purpose is carbonate of potassa, prepared by heating cream of tartar to redness in a covered crucible. (Poggendorff's Annalen, iv. 23.)

Potassium is solid at the ordinary temperature of the atmosphere. At 70° it is somewhat fluid, though its fluidity is not perfect till it is heated to 150°. At 50° it is soft and malleable, and yields like wax to the pressure of the fingers; but it becomes brittle when cooled to 32°. It sublimes at a low red heat, without undergoing any change, provided atmospheric air be completely excluded. Its texture is crystalline, as may be seen by breaking it across while brittle. In colour and lustre it is precisely similar to mercury. At 60° its density is 0.865, so that it is considerably lighter than water. It is quite opaque, and is a good conductor of heat and electricity.

The most prominent chemical property of potassium is its affinity for oxygen gas. It oxidizes rapidly in the air, or by contact with fluids which contain oxygen. On this account it must be preserved either in glass tubes hermetically sealed, or under the surface of liquids, such as naphtha, of which oxygen is not an element.* If heated in the open air, it takes fire, and burns with a purple flame and great evolution of heat. It decomposes water on the instant of touching it, and so much heat is disengaged, that the potassium is inflamed, and burns vividly while swimming upon its surface. The hydrogen unites with a little potassium at the moment of separation; and this compound takes fire as it escapes, and thus augments the brilliancy of the combustion. When potassium is plunged under water, violent reaction ensues, but without light, and pure hydrogen gas is evolved.

The combining weight or equivalent of potassium is easily deducible from the composition of potassa and chloride of potassium, which are admitted to consist of single equivalents of their elements. Gay-Lussac and Thenard, and Davy inferred the composition of potassa from the hydrogen gas evolved, when a known weight of potassium is oxidized under water, the volume of the oxygen which unites with the metal being equal to half the volume of the hydrogen. Berzelius analyzed chloride of potassium by means of nitrate of oxide of silver, and inferred that 39.15 is the equivalent of potassium.

	Potassium.			Equiv.	Formulæ.
Protoxide	39.15	1 eq.+Oxygen	8	1 eq.= 47.15	$K+O$ or $\dot{K}$.
Peroxide	39.15	1 eq.+ do.	24	3 eq.= 63.15	$K+3O$ or $\ddot{K}$.
Chloride	39.15	1 eq.+Chlor.	35.42	1 eq.= 74.57	$K+Cl$ or KCl.
Iodide	39.15	1 eq.+Iodine	126.3	1 eq.=165.45	$K+I$ or KI.
Bromide	39.15	1 eq.+Brom.	78.4	1 eq.=117.55	$K+Br$ or KBr.
Fluoride	39.15	1 eq.+Fluor.	18.68	1 eq.= 57.83	$K+F$ or KF.
Hydurets Carburet	Composition uncertain.				
Sulphuret	39.15	1 eq.+Sulphur	16.1	1 eq.= 55.25	$K+S$ or $\acute{K}S$.
Bisulphuret	39.15	1 eq.+ do.	32.2	2 eq.= 71.35	$K+2S$ or KS^2.
Tersulphuret	39.15	1 eq.+ do.	48.3	3 eq.= 87.45	$K+3S$ or KS^3.
Quadrosulphuret	39.15	1 eq.+ do.	64.4	4 eq.=103.55	$K+4S$ or KS^4.
Quintosulphuret	39.15	1 eq.+ do.	80.5	5 eq.=119.65	$K+5S$ or KS^5.
Phosphurets Seleniurets	Composition and number uncertain.				
Cyanurets	39.15	1 eq.+Cyanog.	26.39	1 eq.= 65.54	$K+Cy$ or KCy.
Sulphycyanuret	39.15	1 eq.+ Bisulph. of Cy.	58.59	1 eq.= 97.74	$K+CyS^2$.

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* Mr. Durand, pharmaceutist of Philadelphia, has ascertained that the essential oil of copaiba is a good liquid for the preservation of potassium. I have used it myself for this purpose, and am satisfied that it is superior to the ordinary naphtha. The brightness of the metal is but slightly impaired, while in common naphtha it becomes covered with a blackish film. Several chemists have used this oil on the recommendation of Mr. Durand, and with satisfactory results.—*Ed.*

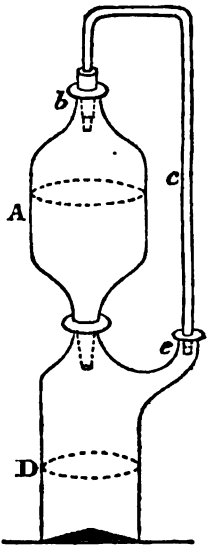
Protoxide of Potassium.—This compound, commonly called *potash* or *potassa*, and by the Germans *kali* (an Arabic word), is always formed when potassium is put into water, or when it is exposed at common temperatures to dry air or oxygen gas. By the former method the protoxide is obtained in combination with water; and in the latter it is anhydrous. In performing the last-mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, is regarded by Berzelius as a distinct oxide; but most chemists admit it to be a mere mixture of potassa and potassium.

Anhydrous potassa can only be prepared by the slow oxidation of potassium, as already mentioned. In its pure state it is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. With a certain portion of that liquid it forms a solid hydrate, the elements of which are united by an affinity so energetic, that no degree of heat hitherto employed can effect their separation. This substance was long regarded as the pure alkali, but it is in reality a *hydrate of potassa*. It is composed of 47.15 parts or one eq. of potassa, and 9 parts or one eq. of water; and its formula is $(K+O) + (H+O)$, or $\dot{K} + \dot{H}$.

Hydrate of potassa is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. It is highly deliquescent, and requires about half its weight of water for solution. It is soluble, likewise, in alcohol. It destroys all animal textures, and on this account is employed in surgery as a caustic. It was formerly called *lapis causticus*, but it is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potassa in a silver or clean iron capsule to the consistence of oil, and then pouring it into moulds. In this state it is impure, containing oxide of iron, together with chloride of potassium, and carbonate and sulphate of potassa. It is purified from these substances by solution in alcohol, and evaporation to the same extent as before in a silver vessel. The operation should be performed expeditiously, in order to prevent, as far as possible, the absorption of carbonic acid. When common caustic potassa of the druggists is dissolved in water, a number of small bubbles of gas are disengaged, which is pure oxygen. Mr. Graham finds its quantity to be variable in different specimens, and to depend apparently on the impurity of the specimen.

The aqueous solution of potassa, *aqua potassæ* of the Pharmacopœia, is prepared by decomposing carbonate of potassa by lime. To effect this object completely, it is advisable to employ equal parts of quicklime and carbonate of potassa. The lime, as soon as it is slaked, is added to the carbonate, dissolved in six or ten times its weight of hot water, and the mixture is boiled briskly in a clean iron vessel for about ten minutes. The liquid, after subsiding, is filtered through a funnel, the throat of which is obstructed by a piece of clean linen. This process is founded on the fact that lime deprives carbonate of potassa of its acid, forming an insoluble carbonate of lime, and setting the pure alkali at liberty. If the decomposition is complete, the filtered solution should not effervesce when neutralized with an acid. Liebig finds that a strong solution of caustic potassa actually deprives carbonate of lime of its acid, and that, from this circumstance, carbonate of potassa cannot be rendered quite caustic by lime, unless diluted with about ten times its weight of water.

As pure potassa absorbs carbonic acid rapidly when freely exposed to the atmosphere, it is desirable to filter its solution in vessels containing as small a quantity of air as possible. This is easily effected by means of the filtering apparatus devised by Mr. Donovan. It consists of two vessels A and D, of equal capacity, and connected with each other as represented in the annexed wood-cut. The neck *b* of the upper vessel contains a tight cork, perforated to admit one end of the glass tube *c*, and the lower extremity of the same vessel terminates in a funnel pipe, which fits into one of the necks of the under vessel D by grinding, luting, or a tight cork. The vessel D is furnished with another neck *e*, which receives the lower end of the tube *c*, the junction being secured by means of a perforated cork, or luting. The throat of the funnel pipe is obstructed by a piece of coarse linen loosely rolled up, and not pressed down into the pipe itself. The solution is then poured in through the mouth at *b*, the cork and tube having been removed; and the first droppings, which are turbid, are not received in the lower vessel. The parts of the apparatus are next joined together, and the filtration may proceed at the slowest rate, without exposure to more air than was contained in the vessels at the beginning of the process. This apparatus should be made of green in preference to white glass; as the pure alkalies act on the former much less than on the latter. (Annals of Philosophy, xxvi. 115.)



The mode by which this apparatus acts scarcely needs explanation. In order that the liquid should descend freely, two conditions are required:—first, that the air above the liquid should have the same elastic force, and therefore exert the same pressure, as that below; and, secondly, as one means of securing the first condition, that the air should have free egress from the lower vessel. Both objects, it is manifest, are accomplished in the filtering apparatus of Mr. Donovan; since for every drop of liquid which descends from the upper to the lower vessel, a corresponding portion of air passes along the tube *c* from the lower vessel to the upper.

Solution of potassa is highly caustic, and its taste intensely acrid. It possesses alkaline properties in an eminent degree, converting the vegetable blue colours to green, and neutralizing the strongest acids. It absorbs carbonic acid gas rapidly, and is consequently employed for withdrawing that substance from gaseous mixtures. For the same reason it should be preserved in well-closed bottles, that it may not absorb carbonic acid from the atmosphere.

Potassa is employed as a reagent in detecting the presence of bodies, and in separating them from each other. The solid hydrate, owing to its strong affinity for water, is used for depriving gases of hygrometric moisture, and is admirably fitted for forming frigorific mixtures. (Page 39.)

Potassa may be distinguished from all other substances by the following characters. 1. If tartaric acid be added in excess to a salt of potassa, dissolved in cold water, and the solution be stirred with a glass rod, a white precipitate, bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. It is precipitated by perchloric acid in the cold, the perchlorate of potassa having nearly the same degree of solubility as the bitartrate. 3. A solution of chloride of platinum causes a yellow precipitate, the double chloride of platinum and potassium. A drop or two of hydrochloric acid should be added at the same time as the test, the mixture be evaporated to dryness at 212°, and a little cold water be afterwards added, when the double chloride is left in the form of small shining yellow crystals. Chloride of platinum dissolved in alcohol often gives an immediate precipitate, which falls of a pale yellow colour. 4. The alcoholic solution of carbazotic acid throws down potassa in yellow crystals of carbazotate of potassa, which is very sparingly soluble.

5. It yields a light gelatinous precipitate, the double fluoride of potassium and silicium, with silicated hydrofluoric acid. Of these tests carbazotic acid is the most delicate in a solution of pure potassa; but when the alkali is combined with a strong acid, the chloride of platinum is preferable.

The following test has been recommended by M. Harkort for distinguishing between potassa and soda in minerals. Oxide of nickel, when fused by the blowpipe flame with borax, gives a brown glass; and this glass, if melted with a mineral containing potassa, becomes blue, an effect which is not produced by the presence of soda.

Peroxide.—When potassium burns in the open air or in oxygen gas, it is converted into an orange-coloured substance, which is peroxide of potassium. It may likewise be formed by conducting oxygen gas over potassa at a red heat; and it is produced in small quantity when potassa is heated in the open air. It is the residue of the decomposition of nitre by heat in metallic vessels, provided the temperature be kept up for a sufficient time.* When the peroxide is put into water, it is resolved into oxygen and potassa, the former of which escapes with effervescence, and the latter is dissolved.

Chloride of Potassium.—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is generated with evolution of hydrogen when potassium is heated in hydrochloric acid gas; and it is the residue after the decomposition of chlorate of potassa by heat. It is formed when potassa is dissolved in a solution of hydrochloric acid, and is deposited by slow evaporation in anhydrous colourless cubic crystals. It has a saline and rather bitter taste, is insoluble in alcohol, and requires for solution 3 parts of water at 60°, and still less of hot water.

Iodide of Potassium.—This compound is formed with evolution of heat and light, when potassium is heated in contact with iodine: it is the sole residue after decomposing iodate of potassa by heat; and by neutralizing potassa with hydriodic acid it is obtained in solution. The simplest process for preparing it in quantity is to add iodine to a hot solution of pure potassa until the alkali is neutralized, when iodide of potassium and iodate of potassa are generated, evaporate to dryness, and expose the dry mass in a platinum crucible to a gentle red heat in order to decompose the iodate. The fused mass is then dissolved out by water and crystallized. Another process is to digest iodine with zinc or iron filings in water, and then decompose the resulting iodide of zinc or iron by a quantity of potassa just sufficient to precipitate the oxide.

Iodide of potassium fuses readily when heated, and rises in vapour at a heat below full redness, especially in an open vessel. It is very soluble in water, requiring only two-thirds of its weight at 60° for solution, and in a moist atmosphere deliquesces. It dissolves also in strong alcohol, even in the cold, and the solution, when evaporated, yields colourless cubic crystals of iodide of potassium.

The commercial iodide is frequently impure, often containing chloride of potassium or sodium, and sulphate or carbonate of potassa, the last sometimes in a very large quantity. It is well to purchase it in crystals, which ought not to deliquesce in a moderately dry air, but when in powder are completely soluble in the strongest alcohol.

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* This fact was ascertained by Dr. Bridges of Philadelphia, in the spring of 1827, while investigating the nature of the gas given off, on the addition of water, from the residue of nitre, after exposure in an iron bottle to a red heat. This gas proved to consist of oxygen nearly pure, and the residue was converted into a solution of hydrate of potassa. These results evidently prove, that the residue in question consists of peroxide of potassium. Dr. Bridges suggests that the employment of this residue might prove convenient to the chemist for obtaining oxygen extemporaneously; as it would be necessary only to add water in order to obtain the gas.—*North American Medical and Surgical Journal,* v. 241.

About the same time that Dr. Bridges made the above observations, similar ones were made by Mr. Phillips in London.—*Annals of Philosophy,* *April* 1827.—*Ed.*

Iodine is freely soluble in water which contains iodide of potassium, a brown solution resulting, which has been thought to arise from potassium uniting with two or more equivalents of iodine. No solid compound of the kind, however, has been obtained.

Bromide of Potassium.—This compound is formed by processes similar to that for preparing the iodide, and is analogous to it in most of its properties. It is very soluble in water, and crystallizes by evaporation in anhydrous cubic crystals, which fuse readily, and decrepitate when heated like sea-salt. It is but slightly soluble in alcohol.

Fluoride of Potassium.—This compound is best formed by nearly saturating hydrofluoric acid with carbonate of potassa, evaporating to dryness in platinum, and igniting to expel any excess of acid. The resulting fluoride has a sharp saline taste, is alkaline to test paper, deliquesces in the air, and dissolves freely in water. On evaporating its solution at a temperature of 100° it may be obtained in cubes or rectangular four-sided prisms, which deliquesce rapidly. The solution acts on glass in which it is kept or evaporated. Heated with silicic acid, it forms a fusible limpid glass, which when cold is opaque and deliquescent. Water dissolves fluoride of potassium, and the silicic acid is left.

Hydrogen and Potassium.—These substances unite in two proportions, forming in one case a solid and in the other a gaseous compound. The latter is produced when hydrate of potassa is decomposed by iron at a white heat; and it appears also to be generated when potassium burns on the surface of water. It inflames spontaneously in air or oxygen gas; but on standing for some hours over mercury, the greater part, if not the whole of the potassium, is deposited.

The solid hyduret of potassium was made by Gay-Lussac and Thenard, by heating potassium in hydrogen gas. It is a gray solid substance, which is readily decomposed by heat or contact with water. It does not inflame spontaneously in oxygen gas.

Carburet of Potassium.—This compound has not been obtained in a pure state; but it is thought to form part of the residue in the preparation of potassium from charcoal (page 294); for on pouring that matter into water, effervescence ensues owing to the escape of carburetted hydrogen gas, and carbonate of potassa is found in solution.

Sulphurets of Potassium.—Potassium unites readily with sulphur by the aid of gentle heat, emitting so much heat that the mass becomes incandescent. The nature of the product depends on the proportions which are employed. The protosulphuret is readily prepared by decomposing sulphate of potassa by charcoal or hydrogen gas at a red heat (page 288). It may be prepared in the moist way by a process which will be mentioned in describing the sulphur-salts.

The *protosulphuret* of potassium fuses below a red heat, and acquires on cooling a crystalline texture. It has a red colour, its taste is at first strongly alkaline and then sulphurous, has an alkaline reaction with test paper, deliquesces on exposure to the air, and is soluble in water and alcohol. Most of the acids decompose it with evolution of hydrosulphuric acid gas, and without any deposite of sulphur. It takes fire when heated before the blowpipe, and quickly acquires a coating of sulphate of potassa, which stops the combustion; but when mixed in fine division with charcoal, it kindles spontaneously, forming a good pyrophorus.

The *bisulphuret* is formed by exposing a saturated solution in alcohol of hydrosulphate of sulphuret of potassium ($KS + HS$), until a pellicle begins to form upon its surface, and then evaporating to dryness without further exposure. The first change consists in oxygen of the air uniting with hydrogen of hydrosulphuric acid, the sulphur of which unites with potassium.

Then the formation of hyposulphurous acid begins; and as the hyposulphite of potassa is insoluble in alcohol, it gives a pellicle on its surface.

The *tersulphuret* is prepared pure by transmitting the vapour of bisulphuret of carbon over carbonate of potassa at a red heat, as long as carbonic acid or carbonic oxide gases are disengaged. It is also formed when carbonate of potassa is heated to low redness with half its weight of sulphur, until the mass appears in tranquil fusion: the oxygen of 3-4ths of the potassa unites with sulphur to form sulphuric acid, which exactly suffices to neutralize 1-4th of the alkali, and all the carbonic acid is evolved as gas.—Thus

4 eq. potassa and 10 eq. sulphur yield 3 eq. tersulphuret & 1 eq. sulphate.
$4(K+O)$ $10S$ $3(K+3S)$ $(K+O)+(S+3O)$.

This is known under the name of *liver of sulphur* (p. 288).

The *quadrosulphuret* is prepared by transmitting the vapour of bisulphuret of carbon over sulphate of potassa at a red heat, until carbonic acid gas ceases to be disengaged; or by conducting the same process with the tersulphuret prepared by the second method, until its sulphuric acid and potassa are decomposed.

The *quintosulphuret* is formed by fusing carbonate of potassa with its own weight of sulphur, the residue containing sulphate of potassa as in preparing the tersulphuret. Each equivalent of potassium is united with five of sulphur, being the highest degree of sulphuration which can be formed by fusion.

These four last sulphurets are deliquescent in the air, have a sulphurous odour, and are soluble in water; and those who consider them to decompose water in dissolving, suppose the formation of corresponding compounds of hydrogen and sulphur. On decomposing the solutions with hydrochloric or sulphuric acid, the changes ensue which have already been explained (page 260). As the solution of the quintosulphuret dissolves sulphur, a still higher degree of sulphuration must probably exist.

Phosphurets of Potassium.—When potassium is heated in phosphuretted hydrogen gas, it takes fire, phosphuret of potassium is formed, and hydrogen set free; and combination is also effected by gently heating phosphorus with potassium. The number and proportion of these compounds have not yet been determined. They decompose water with formation of phosphuretted hydrogen, potassa, and some acid of phosphorus.

Seleniurets of Potassium.—These elements unite when fused together, sometimes with explosive violence, forming a crystalline fusible compound of an iron-gray colour and metallic lustre. It dissolves completely in water, yielding a deep red solution, very similar in taste and odour to solutions of sulphuret of potassium. On adding an acid, hydroselenic acid gas is evolved, and selenium deposited. Solution of potassa dissolves selenium, and gives rise to a seleniuret of potassium and selenite of potassa; and the same compounds are formed when selenium is heated with carbonate of potassa.

Cyanuret of Potassium.—This substance is always produced when animal matters are decomposed by heat along with potassa; but the best mode of preparing it, is to heat anhydrous ferrocyanuret of potassium to redness in an iron bottle, furnished with a tube for the escape of gas, as long as any gas is disengaged. The cyanuret of iron is thus resolved into a carburet of iron and nitrogen, and the former remains mixed with cyanuret of potassium: the latter should be dissolved in the smallest possible quantity of cold water, and the solution, after subsiding in a corked bottle, be rapidly filtered, and brought to dryness in vacuo by means of sulphuric acid.

Cyanuret of potassium is very fusible, bears a strong heat without decomposition, provided air and water are excluded, and may be preserved in a well-stoppered bottle without change. It often crystallizes after fusion in colourless cubes. Exposed to the air it gradually becomes moist, and smells strongly of hydrocyanic acid. Its taste is pungent and alkaline, followed by the flavour of hydrocyanic acid, and it has an alkaline reaction. It is poisonous, acting on animals in the same manner as hydrocyanic acid. In water it is very soluble, and also dissolves, though less readily, in alcohol. Its solution is decomposed by acids, potassa and hydrocyanic acid being generated, a change which is caused even by the carbonic acid of the air. On heating its solution a complex change ensues, during which, from reaction between the elements of water and cyanogen, carbonic acid, hydrocyanic acid, and ammonia are generated.

The impurities which cyanuret of potassium is apt to contain, are ferrocyanuret of potassium and carbonate of potassa. The former may be detected by its forming Prussian blue with sulphate of peroxide of iron, an effect which pure cyanuret of potassium does not occasion; and it may be got rid of by renewed exposure to heat. Carbonate of potassa is present if a solution of the cyanuret gives a precipitate of carbonate of lime in a solution of chloride of calcium; and the cyanuret is purified by solution in boiling alcohol, out of which it separates by evaporation.

Sulphocyanuret of Potassium.—To prepare this compound take anhydrous ferrocyanuret of potassium in powder, mix it with an equal weight of sulphur, and heat the mixture in a porcelain vessel to a strong heat, somewhat short of redness. The mixture speedily fuses, takes fire, and burns briskly for a few minutes, during which it should be well stirred. In this process sulphur unites with 2-3rds of the cyanogen, forming bisulphuret of cyanogen; 1-3rd of the cyanogen is decomposed, yielding bisulphuret of carbon and nitrogen, which escape; and the iron combines with sulphur. On adding water and filtering, a colourless solution is obtained, and on the filter remains sulphuret of iron of a green colour. It often happens that the solution after a few hours becomes red, owing apparently to the presence of sulphocyanuret of iron, the metal of which is oxidized by the oxygen of the air: in that case a quantity of carbonate of potassa should be added, which just suffices to precipitate the iron, and the solution be again filtered. The second process may be prevented, and the product increased, by mixing with the ferrocyanuret of potassium about 1-5th of its weight of pure carbonate of potassa before fusion with sulphur.

Sulphocyanuret of potassium is very fusible, and in close vessels bears a strong heat without decomposition. It has a cool saline taste, similar to that of nitre, deliquesces in the air, is very soluble in water, and is likewise dissolved by alcohol. A hot concentrated solution deposites confused prismatic crystals as it cools. It is quite neutral to test paper, and may be kept even in water without change.

SECTION II.

SODIUM.

Sodium, the *natrium* of the Germans, was discovered in 1807, a few days after the discovery of potassium. The first portions of it were obtained by means of galvanism; but it may be procured in much larger quantity by chemical processes, precisely similar to those described in the last section.

Sodium has a strong metallic lustre, and in colour is very analogous to silver. It is so soft at common temperatures, that it may be formed into leaves by the pressure of the fingers. It fuses at 200°, and rises in vapour at a red heat. Its specific gravity is 0.972.

Sodium soon tarnishes on exposure to the air, though less rapidly than potassium. Like that metal it is instantly oxidized by water, hydrogen gas in temporary union with a little sodium being disengaged. When thrown on cold water, it swims on its surface and is rapidly oxidized, though in general without inflaming; but with hot water it scintillates, or even takes fire. Dr. Ducatel finds that the heat rises high enough for inflammation with cold water, if the sodium be confined to one spot, and the water rest on a non-conducting substance, such as charcoal. (Silliman's Journal, xxv. 90.) In each case, soda is generated, and the water acquires an alkaline reaction.

The composition of soda was determined by the same methods as that of potassa, and agreeably to the observations of Berzelius 23.3 may be taken as the equivalent of sodium. The composition of the compounds of sodium described in this section is as follows:—

	Sodium.					Equiv.	Formulæ.
Protoxide	23.3	1 eq.+	Oxygen	8	1 eq.=	31.3	$Na+O$ or $\dot{Na}$.
Peroxide	46.6	2 eq.+	do.	24	3 eq.=	70.6	$2Na+3O$ or $\ddot{Na}$.
Chloride	23.3	1 eq.+	Chlorine	35.42	1 eq.=	58.72	$Na+Cl$ or $\overline{NaCl}$.
Iodide	23.3	1 eq.+	Iodine	126.3	1 eq.=	149.6	$Na+I$ or NaI.
Bromide	23.3	1 eq.+	Bromine	78.4	1 eq.=	101.7	$Na+Br$ or $NaBr$.
Fluoride	23.3	1 eq.+	Fluorine	18.68	1 eq.=	41.98	$Na+F$ or NaF.
Sulphuret	23.3	1 eq.+	Sulphur	16.1	1 eq.=	39.4	$Na+Sl$ or NaS.
Cyanuret	23.3	1 eq.+	Cyanogen	26.39	1 eq.=	49.69	$Na+Cy$ or $NaCy$.
Sulphocyanuret	23.3	1 eq.+	Cyanogen Sulphur	26.39 32.2	58.59 1 eq.=	81.89	$Na+(Cy+2S)$ or $Na+CyS^2$.

Chloride of soda. Composition uncertain.

Soda.—The protoxide of sodium, commonly called *soda*, and by the Germans *natron*, is formed by the oxidation of sodium in air and water, as potassa is from potassium. In its anhydrous state it is a gray solid, difficult of fusion, and very similar in all its characters to potassa. With water it forms a solid hydrate, easily fusible by heat, which is very caustic, soluble in water and alcohol, has powerful alkaline properties, and in all its chemical relations is exceedingly analogous to potassa. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparation of potassa. The solid hydrate is composed of 31.3 parts or one equivalent of soda, and 9 parts or one equivalent of water.

Soda is readily distinguished from other alkaline bases by the following characters. 1. It yields with sulphuric acid a salt, which by its taste and form is easily recognized as Glauber's salt, or sulphate of soda. 2. All its salts are soluble in water, and are not precipitated by any reagent. 3. On exposing its salts by means of platinum wire to the blowpipe flame, they communicate to it a rich yellow colour.

Peroxide of Sodium.—This compound is formed when sodium is heated to redness in an excess of oxygen gas. It has an orange colour, has neither acid nor alkaline properties, and is resolved by water into soda and oxygen.

Chloride of Sodium.—This compound may be formed directly by burning sodium in chlorine, by heating sodium in hydrochloric acid gas, and by neutralizing soda with hydrochloric acid. It exists as a mineral under the name of *rock salt*, is the chief ingredient of sea-water, and is contained in many saline springs. From these sources are derived the different varieties of common salt, such as rock, bay, fishery, and stoved salt, which differ from each other only in degrees of purity and mode of preparation.

The common varieties of salt, of which rock and bay salt are the purest, always contain small quantities of sulphate of magnesia and lime, and chloride of magnesium. These earths may be precipitated as carbonates by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with hydrochloric acid. On evaporating this solution rapidly, chloride of sodium crystallizes in hollow four-sided pyramids; but it occurs in regular cubic crystals when the solution is allowed to evaporate spontaneously. These crystals contain no water of crystallization, but decrepitate remarkably when heated, owing to the expansion of water mechanically confined within them.

Pure chloride of sodium has an agreeably saline taste. It fuses at a red heat, and becomes a transparent brittle mass on cooling. It deliquesces slightly in a moist atmosphere, but undergoes no change when the air is dry. In pure alcohol it is insoluble. It requires twice and a half its weight of water at 60° for solution, and its solubility is not increased by heat. Hydrous sulphuric acid decomposes it with evolution of hydrochloric acid gas, and formation of sulphate of soda.

The uses of chloride of sodium are well known. Besides its employment in seasoning food, and in preserving meat from putrefaction, a property which when pure it possesses in a high degree, it is used for various purposes in the arts, especially in the formation of hydrochloric acid and chloride of lime.

Iodide of Sodium.—It is obtained pure by processes similar to those for preparing iodide of potassium; but it is contained in sea-water, in many salt springs, and in the residual liquor from kelp (page 228.) It is a neutral compound, deliquescent in the air, soluble in water and alcohol, fuses readily by heat, and is volatile, though in a less degree than iodide of potassium. Evaporated at 123° it crystallizes from its aqueous solution in cubes, which Berzelius found to contain 20.23 per cent. of water.

Bromide of Sodium.—This compound is very analogous to sea-salt, and is associated with it in sea-water and most salt springs. At 86° it crystallizes from its aqueous solution in anhydrous cubes; but at lower temperatures it separates in hexagonal tables, which Mitscherlich found to contain 26.37 per cent. of water, or four equivalents to one eq. of the bromide.

Fluoride of Sodium.—This compound is formed by neutralizing hydrofluoric acid by soda, and by igniting the double fluoride of sodium and silicium, when the fluoride of silicium is expelled. When obtained by the second process, it crystallizes from its aqueous solution in rhomboidal crystals, but is obtained in cubes, its proper form, by a second crystallization: when carbonate of soda is present it crystallizes in octohedrons.

Fluoride of sodium in crystals is anhydrous, is almost insoluble in alcohol, and requires 25 times its weight both of hot and cold water for solution. It attacks glass vessels when evaporated in them, and by fusion unites with silicic acid, forming a glass which is more fusible than the pure fluoride; but water dissolves out the fluoride, and leaves the silicic acid.

Sulphuret of Sodium.—The protosulphuret is obtained by processes similar to those for protosulphuret of potassium, to which in its taste and chemical relations it is very similar. A concentrated solution of it yields hydrated, square, four-sided prisms, which, when heated, fuse in their water of crystallization, and then leave a white anhydrous mass. It deliquesces in the air, is very soluble in water, and is also dissolved, though in a smaller degree, by alcohol. In solution it absorbs oxygen very rapidly from the air, and passes into hyposulphate of soda.

Sodium unites with sulphur in other proportions; but the resulting compounds have not been studied.

According to Gmelin of Tubingen, sulphuret of sodium is the colouring principle of *lapis lazuli*, to which the colour of ultra-marine is owing; and he has succeeded in preparing artificial ultra-marine by heating sulphuret of sodium with a mixture of silicic acid and alumina. (An. de Ch. et de Ph. xxxvii. 409.)

Chloride of Soda.—This compound has lately acquired the attention of scientific men under the name of Labarraque's *disinfecting soda liquid*, which was announced by M. Labarraque as a compound of chlorine and soda, analogous to the well-known bleaching powder, chloride of lime. The nature of this liquid has been since investigated by Mr. Phillips and Mr. Faraday, especially by the latter; and it appears from the experiments of this chemist, that while chloride of soda is the active ingredient, its properties are considerably modified by the presence of carbonate of soda. (Quarterly Journal of Science, N. S. ii. 84.)

Pure chloride of soda is easily prepared by transmitting to saturation a current of chlorine gas into a cold and rather dilute solution of caustic soda. Common carbonate of soda may be substituted for the pure alkali; but considerable excess of chlorine must then be employed in order to displace the whole of the carbonic acid. It may also be formed easily, cheaply, and of uniform strength, by decomposing chloride of lime with carbonate of soda, as proposed by M. Payen. (Quart. Journal of Science, N. S. i. 236.) However prepared, its properties are the same. As its constituents are retained in combination by a feeble affinity, the compound is easily destroyed. It emits the odour of chlorine, and possesses the bleaching properties of that substance in a very high degree. When kept in open vessels, it is slowly decomposed by the carbonic acid of the atmosphere with evolution of chlorine; and the change is more rapid in air charged with putrid effluvia, because the carbonic acid produced during putrefaction promotes the decomposition of the chloride. On this, as was proved by M. Gaultier de Chaubry, depends the efficacy of an alkaline chloride in purifying air loaded with putrescent exhalations. When the solution is heated to the boiling point, or concentrated by means of heat, the chloride undergoes a change previously explained (page 211), and is converted into chlorate of soda and chloride of sodium.

Chloride of soda may be employed in bleaching, and for all purposes to which chlorine gas or its solution was formerly applied. It is now much used in removing the offensive odour arising from drains, sewers, or all kinds of animal matter in a state of putrefaction. Bodies disinterred for the purpose of judicial inquiry, or parts of the body advanced in putrefaction, may by its means be rendered fit for examination; and it is employed in surgical practice for destroying the fetor of malignant ulcers. Clothes worn by persons during pestilential diseases are disinfected by being washed with this compound.

It is also used in fumigating the chambers of the sick; for the disengagement of chlorine is so gradual, that it does not prove injurious or annoying to the patient. In all these instances chlorine appears actually to decompose noxious exhalations by uniting with the elements of which they consist, and especially with hydrogen.

In preparing the disinfecting liquid of Labarraque, it is necessary to be exact in the proportion of the ingredients employed. The quantities used by Mr. Faraday, founded on the directions of Labarraque, are the following. He dissolved 2800 grains of crystallized carbonate of soda in 1.28 pints of water, and through the solution, contained in Woulfe's apparatus, was transmitted the chlorine evolved from a mixture of 967 grains of sea-salt and 750 grains of peroxide of manganese, when acted on by 967 grains of sulphuric acid, diluted with 750 grains of water. In order to remove any accompanying hydrochloric acid gas, the chlorine before reaching the soda was conducted through pure water, by which means nearly a third part was dissolved, but the remaining two-thirds were fully sufficient for the purpose. The gas was readily absorbed by the solution, and from the beginning to the end of the process, not a particle of carbonic acid gas was evolved; whereas, by employing an excess of chlorine, the carbonic acid may be entirely expelled.

The solution thus prepared has all the characters of Labarraque's soda liquid. Its colour is pale yellow, and it has but a slight odour of chlorine. Its taste is at first sharp, saline, and scarcely at all alkaline; but it produces a persisting biting effect upon the tongue. It first reddens and then destroys the colour of turmeric paper. When boiled it does not give out chlorine, nor is its bleaching power perceptibly impaired; and if carefully evaporated, it yields a mass of damp crystals, which, when re-dissolved, bleach almost as powerfully as the original liquid. When rapidly evaporated to dryness, the residue contains scarcely any chlorate of soda or chloride of sodium; but it has nevertheless lost more than half of its bleaching power, and, therefore, chlorine must have been evolved during the evaporation. The solution deteriorates gradually by keeping, chloric acid and chloride of sodium being generated. When allowed to evaporate spontaneously, chlorine gas is gradually evolved, and crystals of carbonate of soda remain.

In some respects the nature of this liquid is still obscure; but from the preceding facts, drawn from the essay of Mr. Faraday, two points seem to be established. First, that the liquid contains chlorine, carbonic acid, and soda. Secondly, that the chlorine is not simply combined either with water or soda; for by boiling, the gas is neither expelled as it would be from an aqueous solution, nor does the liquid yield chloric acid and chloride of sodium as when pure chloride of soda is heated. It may perhaps be regarded as a compound of chloride and bicarbonate of soda. Its production may be conceived by supposing, that when chlorine is introduced in due quantity into a solution of carbonate of soda, it combines with half of the alkali, while the remainder, with all the carbonic acid, constitutes bicarbonate of soda. Should this salt unite, though by a feeble affinity, with chloride of soda, both may thence derive a degree of permanence which neither singly possesses. During spontaneous evaporation, the tendency of the common carbonate to crystallize may occasion its reproduction, and the disengagement of chlorine. Those remarks, however, are merely speculative.

SECTION III.

LITHIUM.

Davy succeeded by means of galvanism in obtaining from lithia a white-coloured metal like sodium; but it was oxidized, and thus reconverted into lithia, with such rapidity that its properties could not be farther examined. Its equivalent, inferred from the composition of sulphate of lithia by Stromeyer and Thomson, is 10; but the accuracy of this estimate is rendered doubtful by the experiments of M. Herrman, according to which 6 is a nearer estimate. The compounds of lithium described in this section are thus constituted:—

	Lithium.			Equiv.	Formulæ.
Lithia .	10 1 eq.	+ Oxygen .	8	1 eq. = 18	L + O or $\dot{L}$.
Chloride .	10 1 eq.	+ Chlorine .	35.42	1 eq. = 45.42	L + Cl or LCl.
Fluoride .	10 1 eq.	+ Fluorine .	18.68	1 eq. = 28.68	L + F or LF.

Lithia.—This, the only known oxide of lithium, was discovered in 1818 by M. Arfwedson (An. de Ch. et de Ph. x.) in a mineral called *petalite;* and its presence has since been detected in spodumene, lepidolite, and in several varieties of mica. Berzelius has found it also in the waters of Carlsbad in Bohemia. From the circumstance of its having been first obtained from an earthy mineral, Arfwedson gave it the name of *lithion*, (from λίθειος, *lapideus*,) a term since changed in this country to *lithia*. It has hitherto been procured in small quantity only, because spodumene and petalite are rare, and do not contain more than 6 or 8 per cent. of the alkali. It is combined in these two minerals with silicic acid and alumina; whereas potassa is likewise present in lepidolite and lithion-mica, and, therefore, lithia should be prepared solely from the former.

The best process for preparing lithia is that which was suggested by Berzelius. One part of petalite or spodumene, in fine powder, is mixed intimately with two parts of fluor spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silicic acid of the mineral is attacked by hydrofluoric acid, and dissipated in the form of fluosilicic gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina: it is then filtered and evaporated to dryness, and the dry mass heated to redness to expel the sulphate of ammonia. The residue is pure sulphate of lithia.*

Lithia, in its alkalinity, in forming a hydrate with water, and in its chemical relations, is closely allied to potassa and soda. It is distinguished from them by its greater neutralizing power, by forming sparingly soluble compounds with carbonic and phosphoric acids, and by its salts, when heated on platinum wire before the blowpipe, tinging the flame of a red colour. Also, when fused on platinum foil, it attacks that metal and leaves a dull yellow trace round the spot where it lay. It is distinguished from baryta, strontia, and lime, by forming soluble salts with sulphuric and oxalic acids, and from magnesia by its carbonate, though sparingly soluble in water, forming with it a solution which has an alkaline reaction.

Chloride of Lithium.—It is readily obtained by dissolving lithia or its carbonate in hydrochloric acid. Like the chlorides of sodium and potassium, it yields by evaporation in a warm place colourless, anhydrous, cubic crystals, which differ from those chlorides in being very deliquescent, dissolving freely in alcohol as well as water, and in its alcoholic solution burning with a red flame.

The iodide and bromide of lithium have not been examined.

Fluoride of Lithium.—This is a fusible compound, prepared by dissolving lithia in hydrofluoric acid, and possesses about the same solubility in water as the carbonate.

CLASS I.

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION IV.

BARIUM.

Davy discovered *barium*, the metallic base of baryta, in the year 1808, by a process suggested by Berzelius and Pontin. It consists in forming carbonate of baryta into a paste with water, placing a globule of mercury in a little hollow made in its surface, and laying the paste on a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was in contact with the mercury. The baryta was decomposed, and its barium combined with mercury. This amalgam was then heated in a vessel free from air, by which means the mercury was expelled, and barium obtained in a pure form.

Barium, thus procured, is of a dark gray colour, with a lustre inferior to cast iron. It is far denser than water, for it sinks rapidly in strong sulphuric acid. It attracts oxygen with avidity from the air, and in doing so yields a white powder, which is baryta. It effervesces strongly, from the escape of hydrogen gas, when thrown into water, and a solution of baryta is produced. It has hitherto been obtained in very minute quantities, and consequently its properties have not been determined with precision.

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* The sulphate of lithia may be decomposed by acetate of baryta, and the acetate of lithia thus obtained, by exposure to a red heat, is converted into the carbonate. The carbonate may then be brought to the state of a caustic hydrate by the action of lime in the usual manner.—*Ed.*

The equivalent of barium, deduced from an analysis of the chloride by Berzelius and myself, is 68.7. The composition of its compounds described in this section is as follows:—

	Barium.		Equiv.	Formulæ.
Protoxide	68.7	1 eq.+Oxygen 8	1 eq.= 76.7	$Ba+O$ or $\dot{Ba}$.
Peroxide	68.7	1 eq.+Ditto 16	2 eq.= 84.7	$Ba+2O$ or $\ddot{Ba}$.
Chloride	68.7	1 eq.+Chlorin. 35.42	1 eq.=104.12	$Ba+Cl$ or $BaCl$.
Iodide	68.7	1 eq.+Iodine 126.3	1 eq.=195	$Ba+I$ or BaI.
Bromide	68.7	1 eq.+Bromine 78.4	1 eq.=147.1	$Ba+Br$ or $BaBr$.
Fluoride	68.7	1 eq.+Flu'rine 18.68	1 eq.= 87.38	$Ba+F$ or BaF.
Sulphuret	68.7	1 eq.+Sulphur 16.1	1 eq.= 84.8	$Ba+S$ or BaS.
Cyanuret	68.7	1 eq.+Cyanog. 26.39	1 eq.= 95.09	$Ba+(C^2N)$ or $BaCy$.
Sulphocy.	68.7	1 eq.+ { Cyanog. 26.39 1 eq. Sulphur 32.2 2 eq. }	=127.29	$Ba+(C^2N+2S.)$ or $Ba+CyS^2$.

Protoxide of Barium.—*Barytes*, or *Baryta*, so called from the great density of its compounds, (from βαρὺς, heavy,) was discovered in the year 1774 by Scheele. It is the sole production of the oxidation of barium in air and water. It may be prepared by decomposing nitrate of baryta at a red heat; or by exposing carbonate of baryta contained in a black-lead crucible to an intense white heat, a process which succeeds much better when the carbonate is intimately mixed with charcoal. Baryta is a gray powder, the specific gravity of which is about 4. It requires a very high temperature for fusion. It has a sharp caustic alkaline taste, converts vegetable blue colours to green, and neutralizes the strongest acids. Its alkalinity, therefore, is equally distinct as that of potassa or soda; but it is much less caustic and less soluble in water than those alkalies. In pure alcohol it is insoluble. It has an exceedingly strong affinity for water. When mixed with that liquid it slakes in the same manner as quicklime, but with the evolution of a more intense heat, which, according to Döbereiner. sometimes amounts to luminousness. The result is a white bulky hydrate, fusible at a red heat, and which bears the highest temperature of a smith's forge without parting with its water. It is composed of 76.7 parts or one equivalent of baryta, and 9 parts or one equivalent of water.

Hydrate of baryta dissolves in three times its weight of boiling water, and in twenty parts of water at the temperature of 60° F. (Davy.) A saturated solution of baryta in boiling water deposites, in cooling, transparent, flattened prismatic crystals, which are composed, according to Dr. Dalton, of 76.7 parts or one equivalent of baryta, and 180 parts or twenty equivalents of water.

The aqueous solution of baryta is an excellent test of the presence of carbonic acid in the atmosphere or in other gaseous mixtures. The carbonic acid unites with the baryta, and a white insoluble precipitate, carbonate of baryta, subsides.

Baryta is distinguished from all other substances by the following characters. 1. By dissolving in water and forming an alkaline solution. 2. By all its soluble salts being precipitated as white carbonate of baryta by akaline carbonates, and as sulphate of baryta, which is insoluble both in acid and alkaline solutions, by sulphuric acid or any soluble sulphate. 3. By the characters of chloride of barium, formed by the action of hydrochloric acid on baryta.

The readiest method of preparing the soluble salts of baryta is by dissolving the carbonate in dilute acid. All of its soluble salts are poisonous; and the carbonate, from being dissolved by the juices of the stomach, likewise acts as a poison.

The sulphate, from its insolubility, is inert.

Peroxide of Barium.—This oxide, which is used by Thenard in preparing peroxide of hydrogen, may be formed by conducting dry oxygen gas over pure baryta at a low red heat. A still easier process, lately given by Wöhler and Liebig, is to heat pure baryta to low redness in a platinum crucible, and then gradually to add chlorate of potassa in the ratio of about one part of the latter to four of the former. The oxygen of the chlorate goes over to the baryta, and chloride of potassium is generated. Cold water afterwards removes the chloride, and the peroxide of barium is left as a hydrate with six equivalents of water, its formula being $\ddot{\mathrm{Ba}}+6\mathrm{Aq}$.

Chloride of Barium.—It is generated when chlorine gas is conducted over baryta at a red heat, oxygen gas being disengaged; but it is most conveniently prepared by dissolving carbonate of baryta in hydrochloric acid diluted with about three times its weight of water, or by decomposing a solution of sulphuret of barium with hydrochloric acid. On concentrating its solution, the chloride crystallizes on cooling in flat four-sided tables bevelled at the edges, very like crystals of heavy spar. These crystals consist of 104.12 parts or one eq. of chloride of barium, and 18 parts or two eq. of water, its formula being $\mathrm{BaCl}+2\mathrm{Aq}$. They do not change in ordinary states of the air; but in a very dry atmosphere at 60° they lose all their water, and recover it again in a moist air. They are still more rapidly rendered anhydrous at 212°, and fusion ensues at a full red heat. They are insoluble in strong alcohol: 100 parts of water dissolve 43.5 at 60°, and 78 at 222°, which is the boiling point of the solution.

Iodide of Barium.—This compound may be formed in the same way as iodide of potassium. It is very soluble in water, and crystallizes in small colourless needles, which deliquesce slightly. On exposure to the air a portion of carbonate of baryta is formed and iodine set free, which probably forms a periodide of barium.

Bromide of Barium.—It was prepared by M. Henry, jun., who has examined it, by boiling protobromide of iron with moist carbonate of baryta in excess, evaporating the filtered solution, and heating the residue to redness. The product crystallizes by careful evaporation in white rhombic prisms, which have a bitter taste, are slightly deliquescent, and are soluble in water and alcohol.

Fluoride of Barium.—On digesting recently precipitated and moist carbonate of baryta in hydrofluoric acid, carbonic acid is expelled, and fluoride of barium collects in the form of a white powder, which bears a red heat without decomposition. It is sparingly soluble in water, and by evaporation separates in crystalline grains. It is soluble in nitric and hydrochloric acids.

Sulphuret of Barium.—This compound may be formed by transmitting dry hydrosulphuric acid gas over pure baryta at a red heat; and by the action of hydrogen gas or charcoal on sulphate of baryta (page 288.) The easiest process is to mix sulphate of baryta in fine powder into a paste with an equal volume of flour, place it in a Hessian crucible on which a cover is luted, and expose it to a white heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass, the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration.

Protosulphuret of barium is very soluble in hot water, and the solution if saturated deposites colourless crystals on cooling, which are sulphuret of barium with water of crystallization. The solution has a sulphurous odour, and absorbs oxygen and carbonic acid from the air, yielding carbonate and hyposulphite of baryta. Boiled with sulphur it yields a yellow solution, and contains a persulphuret of barium.

Sulphuret of barium supplies a ready mode of obtaining pure baryta and its salts, when the carbonate cannot be obtained. Thus its solution, boiled with black oxide of copper until it ceases to precipitate a salt of lead black, yields pure baryta, which should be filtered while hot to separate the sulphuret of copper: it is apt to retain traces of oxide of copper. With a solution of carbonate of potassa, carbonate of baryta falls, and sulphuret of potassium remains in solution; and with hydrochloric acid it interchanges elements, by which hydrosulphuric acid and chloride of barium are formed.

Cyanuret of Barium.—It is formed by the action of hydrocyanic acid on baryta, or by heating ferrocyanuret of barium as in preparing cyanuret of potassium (page 300). It is but slightly soluble in water, has an alkaline reaction, and is decomposed by the carbonic acid of the air.

Sulphocyanuret of Barium is obtained in the same way as the sulphocyanuret of potassium. It is very soluble in water, crystallizes in brilliant needles, and is slightly deliquescent.

SECTION V.

STRONTIUM.

Davy discovered the metallic base of strontia, called *strontium*, by a process analogous to that described in the last section. All that is known respecting its properties is, that it is a heavy metal, similar in appearance to barium, that it decomposes water with evolution of hydrogen gas, and oxidizes quickly in the air, being converted in both cases into strontia, which is the protoxide of the metal.

The equivalent of strontium, deduced from the experiments of Stromeyer, is 43.8. The composition of its several compounds described in this section is as follows:—

	Strontium.				Equiv.	Formulæ.
Protoxide	43.8	1 eq.+Oxygen	8	1 eq.=	51.8	Sr+O or $\dot{\text{Sr}}$.
Peroxide	43.8	1 eq.+ do.	16	2 eq.=	59.8	Sr+2O or $\ddot{\text{Sr}}$.
Chloride	43.8	1 eq.+Chlorine	35.42	1 eq.=	79.22	Sr+Cl or SrCl.
Iodide	43.8	1 eq.+Iodine	126.3	1 eq.=	170.1	Sr+I or SrI.
Fluoride	43.8	1 eq.+Fluorine	18.68	1 eq.=	62.48	Sr+F or SrF.
Sulphuret	43.8	1 eq.+Sulphur	16.1	1 eq.=	59.9	Sr+S or SrS.

Protoxide of Strontium.—From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Dr. Crawford, however, and M. Sulzer noticed a difference between them; but the existence of strontia was first established with certainty in the year 1792 by Dr. Hope,[*] and the discovery was made about the same time by Klaproth.[†] It was originally extracted from strontianite, native carbonate of strontia, a mineral found at Strontian in Scotland; and hence the origin of the term *strontites* or *strontia*, by which the earth itself is designated.

Pure strontia may be prepared from nitrate and carbonate of strontia, in the same manner as baryta. It resembles this earth in appearance, in infusibility, and in possessing distinct alkaline properties. It slakes when mixed with water, causing intense heat, and forming a white solid hydrate, which consists of 51.8 parts or one equivalent of strontia, and 9 parts or one equivalent of water. Hydrate of strontia fuses readily at a red heat, but sustains the strongest heat of a wind furnace without decomposition. It is insoluble in alcohol. Boiling water dissolves it freely, and a hot saturated solution, on cooling, deposites transparent crystals in the form of thin quadrangular tables, which consist of one eq. of strontia and twelve eq. of water. They are converted by heat into the protohydrate. They require fifty times their weight of water at 60° for solution, and twice their weight at 212° F. (Dalton.)

The solution of strontia has a caustic taste and alkaline reaction. Like the solution of baryta it is a delicate test of the presence of carbonic acid in air or other gaseous mixtures, forming with it the insoluble carbonate of strontia.

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[*] Edin. Philos. Trans. iv. 3.

[†] Klaproth's Contributions, i.

The salts of strontia are best prepared from the native carbonate. Like those of baryta, they are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. But sulphate of strontia is less insoluble than sulphate of baryta: on adding sulphate of soda in excess to a barytic solution, baryta cannot afterwards be found in the liquid by any precipitant; but when strontia is thus treated, so much sulphate of strontia remains in solution, that the filtered liquid yields a white precipitate with carbonate of soda. The salts of strontia are not poisonous; and most of them, when heated on platinum wire before the blowpipe, communicate to the flame a red tint.

Peroxide of Strontium is prepared in the same way as peroxide of barium, and like it, is resolved by dilute acids into baryta and oxygen, the latter of which forms peroxide of hydrogen with the water.

Chloride of Strontium.—This compound is formed by processes similar to those for preparing chloride of barium, and crystallizes from its solution in colourless prismatic crystals, which deliquesce in a moist atmosphere, require only twice their weight of water at 60° for solution, and still less of boiling water, and are soluble in alcohol. The alcoholic solution, when set on fire, burns with a red flame. These characters afford a certain mode of distinguishing strontia from baryta. The crystals consist of 79.22 parts or one eq. of chloride of strontium, and 81 parts or nine eq. of water, which are expelled by heat. The anhydrous chloride fuses at a red heat, and yields a white crystalline brittle mass on cooling.

Iodide of Strontium may be prepared in the same manner as that of barium. It is very soluble in water, and fuses without decomposition in close vessels; but when heated to redness in the open air, iodine escapes, and strontia is generated.

Fluoride of Strontium is obtained in the same way as fluoride of barium, and is a white powder of sparing solubility.

Protosulphuret of Strontium is similar in its properties and mode of preparation to sulphuret of barium, and may be applied to similar uses. Strontium also combines with more than one equivalent of sulphur, but these compounds have not been examined.

SECTION VI.

CALCIUM.

The existence of calcium, the metallic base of lime, was demonstrated by Sir H. Davy by a process similar to that described in the section on barium. It is of a whiter colour than barium or strontium, and is converted into lime by being oxidized. Its other properties are unknown.

According to the analysis of chloride of calcium by Berzelius, the equivalent of calcium is 20.5. Its compounds described in this section are composed as follows:—

	Calcium.				Equiv.	Formulæ.
Protoxide .	20.5	1 eq.+Oxygen	8	1 eq.=	28.5	$Ca+O$ or $\dot{Ca}$.
Peroxide .	20.5	1 eq.+ do.	16	2 eq.=	36.5	$Ca+2O$ or $\ddot{Ca}$.
Chloride .	20.5	1 eq.+Chlorine	35.42	1 eq.=	55.92	$Ca+Cl$ or $CaCl$.
Iodide . .	20.5	1 eq.+Iodine	126.3	1 eq.=	146.8	$Ca+I$ or CaI.
Bromide .	20.5	1 eq.+Bromine	78.4	1 eq.=	98.9	$Ca+Br$ or $CaBr$.
Fluoride .	20.5	1 eq.+Fluorine	18.68	1 eq.=	39.18	$Ca+F$ or CaF.
Sulphuret .	20.5	1 eq.+Sulphur	16.1	1 eq.=	36.6	$Ca+S$ or CaS.
Bisulphuret .	20.5	1 eq.+ do.	32.2	2 eq.=	52.7	$Ca+2S$ or CaS_2.
Quintosulphuret	20.5	1 eq.+ do.	80.5	5 eq.=	101	$Ca+5S$ or CaS_5.
Phosphuret	20.5	1 eq.+Phosph.	15.7	1 eq.=	36.2	$Ca+P$ or CaP.
Chloride of lime	Lime 28.5	1 eq.+Chlorine	35.42	1 eq.=	63.92	$\dot{Ca}+Cl$ or $\dot{Ca}Cl$.

Protoxide of Calcium.—This compound, commonly known by the name of *lime* and *quicklime*, is obtained by exposing carbonate of lime to a strong red heat, so as to expel its carbonic acid. If lime of great purity is required, it should be prepared from pure carbonate of lime, such as Iceland spar or Carrara marble; but in burning lime in lime-kilns for making mortar, common limestone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. (Page 190.)

Lime is a brittle white earthy solid, the specific gravity of which is about 2.3. It phosphoresces powerfully when heated to full redness, a property which it possesses in common with strontia and baryta. It is one of the most infusible bodies known; fusing with difficulty, even by the heat of the oxy-hydrogen blowpipe. It has a powerful affinity for water, and the combination is attended with great increase of temperature, and formation of a white bulky hydrate, which is composed of 28.5 parts or one equivalent of lime, and 9 parts or one equivalent of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrates of strontia and baryta in parting with its water at a red heat.

Hydrate of lime is dissolved very sparingly by water, and it is a singular fact, first noticed I believe by Dalton, that it is more soluble in cold than in hot water. Thus he found that one grain of lime requires for solution

778	grains of water	. . . at	60° F.
972	do.	. . .	130
1270	do.	. . .	212

And, consequently, on heating a solution of lime, or *lime-water*, which has been prepared in the cold, deposition of lime ensues. This fact was determined experimentally by Mr. Phillips, who has likewise observed that water at 32° is capable of dissolving twice as much lime as at 212° F. Owing to this circumstance, pure lime cannot be made to crystallize in the same manner as baryta or strontia; but Gay-Lussac succeeded in obtaining crystals of lime by evaporating lime-water under the exhausted receiver of an air-pump by means of sulphuric acid. Small transparent crystals, in the form of regular hexahedrons, were deposited, which consist of water and lime in the same proportion as in the hydrate above mentioned.

Lime-water is prepared by mixing hydrate of lime with water, agitating the mixture repeatedly, and then setting it aside in a well-stopped bottle until the undissolved parts shall have subsided. The substance called *milk* or *cream* of lime is made by mixing hydrate of lime with a sufficient quantity of water to give it the liquid form;—it is merely lime-water in which hydrate of lime is mechanically suspended.

Lime-water has a harsh acrid taste, and converts vegetable blue colours to green.—It agrees, therefore, with baryta and strontia in possessing distinct alkaline properties. Like the solutions of these earths, it has a strong affinity for carbonic acid, and forms with it an insoluble carbonate. On this account lime-water should be carefully protected from the air. For the same reason, lime-water is rendered turbid by a solution of carbonic acid; but on adding a large quantity of the acid, the transparency of the solution is completely restored, because carbonate of lime is soluble in an excess of carbonic acid. The action of this acid on the solutions of baryta and strontia is precisely similar.

The salts of lime, which are easily prepared by the action of acids on pure marble, are in many respects similarly affected by reagents, as those of baryta and strontia. They are precipitated, for example, by alkaline carbonates. Sulphuric acid and soluble sulphates likewise precipitate lime from a moderately strong solution. But sulphate of lime has a considerable degree of solubility. Thus, a dilute solution of a salt of lime is not precipitated at all by sulphuric acid; and when the sulphate of lime is separated, it may be redissolved by the addition of nitric acid.

The most delicate test of the presence of lime is oxalate of ammonia or potassa; for of all the salts of lime, the oxalate is the most insoluble in water. This serves to distinguish lime from most substances, though not from baryta and strontia; because the oxalates of baryta and strontia, especially the latter, are likewise sparingly soluble. All these oxalates dissolve readily in water acidulated with nitric or hydrochloric acid. It is distinguished from baryta and strontia by the fact, that nitrate of lime yields prismatic crystals by evaporation, is deliquescent in a high degree, and very soluble in alcohol; while the nitrates of baryta and strontia crystallize in regular octohedrons or segments of the octohedron, undergo no change on exposure to the air, except when it is very moist, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blowpipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

Peroxide of Calcium.—This oxide is prepared in the same way as peroxide of barium, and is similar to it in its properties.

Chloride of Calcium.—This compound exists in sea-water and in many saline springs, is the residue of the process for preparing ammonia, and is readily formed by dissolving marble or chalk in hydrochloric acid. On evaporating its solution to the consistence of a syrup, the chloride crystallizes on cooling in irregular, colourless prismatic crystals, which consist of 55.92 parts or one eq. of chloride of calcium, and 54 parts or six eq. of water. By heat it loses its water, and at a gentle red heat fuses; but on exposure to the air it rapidly recovers its water of crystallization and then deliquesces. Owing to its strong affinity for water, it is much used for frigorific mixtures with snow; but for this purpose the hydrous chloride is preferable, as prepared by evaporating its solution so far that the whole becomes a solid mass on removal from the fire, reducing it when cold quickly to powder, and preserving it in bottles closed with great care. Chloride of calcium is very soluble in alcohol, and forms with it a definite compound.

Iodide of Calcium.—This compound may be prepared by digesting hydrate of lime with protiodide of iron. It is deliquescent and very soluble in water, sustains a red heat unchanged in close vessels, but when heated in the open air, its iodine is replaced by oxygen, and lime remains. The solution of iodide of calcium dissolves a large quantity of iodine, and on evaporating the brown solution in vacuo above a vessel with dry carbonate of potassa, a periodide of calcium crystallizes in large black prisms of a metallic lustre.

Bromide of Calcium.—It was prepared by M. Henry by digesting hydrate of lime with a solution of protobromide of iron, and crystallizes in acicular crystals which are very deliquescent, and extremely soluble in alcohol and water. It is very analogous in taste and properties to chloride of calcium, fuses by heat, but in open vessels suffers partial decomposition.

Fluoride of Calcium.—This is a natural product, which frequently accompanies metallic ores, especially those of lead and tin, often occurs in cubic crystals, and is well known under the name of *fluor* or *Derbyshire spar.* The crystals found in the lead mines of Derbyshire are remarkable for the largeness of their size, the regularity of their form, and the variety and beauty of their colours. It may be prepared artificially by digesting moist, recently precipitated, carbonate of lime in an excess of hydrofluoric acid; or by mixing a solution of chloride of calcium with fluoride of potassium or sodium. As prepared in the latter mode, it is a bulky gelatinous mass, which it is very difficult to wash; whereas the former method gives it in the state of a granular white powder, which may be washed with ease.

Fluoride of calcium fuses at a red heat without farther change. It is insoluble in water, slightly soluble in hot diluted hydrochloric acid, and is decomposed by sulphuric acid aided by gentle heat (page 238). It is in a small degree decomposed by boiling nitric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are generated.

Fluor spar is much used in forming vases, as a flux in metallurgic processes, and in the preparation of hydrofluoric acid.

Protosulphuret of Calcium.—This compound may be prepared by reduction from the sulphate by hydrogen or charcoal, and when pure is white with a reddish tint, and is very sparingly soluble in water. It has the property, in common with sulphuret of barium, of being phosphorescent after exposure to light, and appears to be the essential ingredient of Canton's phosphorus (page 69).

When 3 parts of slaked lime, 1 of sulphur, and 20 of water, are boiled together for an hour, and the solution, without separation from the sediment, is set aside in a corked flask for a few days, a copious deposite of orange-coloured crystals is deposited, which, when slowly formed, are flat quadrilateral prisms. These, from the analysis of Herschel, appear to be *bisulphuret of calcium* with three eq. of water. They are decomposed by exposure to the air, and are of sparing solubility in water.

When either of the foregoing sulphurets is boiled in water along with sulphur, a yellow solution is formed containing calcium combined with five equivalents of sulphur.

Phosphuret of Calcium.—It is formed by passing the vapour of phosphorus over fragments of quicklime at a low red heat; when a brown matter is formed, consisting of phosphate of lime and phosphuret of calcium When put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated.

Chloride of Lime.—This compound, commonly called *oxymuriate of lime*, or *bleaching powder*, is prepared by exposing thin strata of recently slaked lime, in fine powder, to an atmosphere of chlorine. The gas is absorbed in large quantity, and combines directly with the lime.

Chloride of lime is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime, retaining a small quantity of chlorine. The aqueous solution, when exposed to the atmosphere, is gradually decomposed; chlorine is set free, and carbonate of lime generated. On boiling the liquid, chloride of calcium, and, I presume, chlorate of lime are formed; and by long keeping, the dry chloride appears to undergo a similar change, at least chloride of calcium is produced in large quantity. Chloride of lime is also decomposed by a strong heat: at first, chlorine is evolved; but pure oxygen is afterwards disengaged, and chloride of calcium remains in the retort.

The composition of chloride of lime was first carefully investigated by Dalton,* and it has since been analyzed by Thomson,† Welter,‡ and Ure.§ The three first mentioned chemists infer from their researches that bleaching powder is a hydrated *subchloride* or *dichloride* of lime, in which one equivalent of chlorine is united with two equivalents of lime. They are also of opinion, that on mixing this dichloride with water, the chloride is dissolved, and one equivalent of lime separated as an insoluble powder. Dr. Ure, on the contrary, denies that bleaching powder is a dichloride, and maintains that the elements of this powder do not constitute a regular atomic combination. He found that the quantity of chlorine absorbed by hydrate of lime is variable, depending not only on the pressure and degree of exposure, but on the quantity of water present. From these experiments it appears that the commercial bleaching powder is essentially a chloride with single equivalents of its elements, but mixed with variable quantities of hydrate of lime.

Several methods have been proposed for estimating the value of different specimens of chloride of lime. Perhaps the most convenient for the artist is that of Welter, which consists in ascertaining the power of the bleaching liquid to deprive a solution of indigo of known strength of its colour; and directions have been drawn up by Gay-Lussac for enabling manufacturers to employ this method with accuracy. (Annals of Philosophy, xxiv. 218.) For analytical purposes, the best method is to decompose chloride of lime, confined in a glass tube over mercury, by means of hydrochloric acid. Chloride of calcium is generated, and the chlorine being set free, its quantity may easily be measured.

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* Annals of Philosophy, i. 15, and ii. 6. † Ibid. xv. 401.

‡ An. de Ch. et de Ph. vol. viii. § Quarterly Journal, xiii. 1.

SECTION VII.

MAGNESIUM.

The galvanic researches of Sir H. Davy demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. It was prepared by M. Bussy in the year 1830 by the action of potassium on chloride of magnesium. For this purpose five or six pieces of potassium, of the size of peas, were introduced into a glass tube, the sealed extremity of which was bent into the form of a retort, and upon the potassium were laid fragments of chloride of magnesium. The latter being then heated to near its point of fusion, a lamp was applied to the potassium, and its vapour transmitted through the mass of heated chloride. Vivid incandescence immediately took place, and on putting the mass, after cooling, into water, the chloride of potassium with undecomposed chloride of magnesium was dissolved, and metallic magnesium subsided. These results have been since confirmed by Liebig. (An. de Ch. et de Ph. xlvi. 435.)

Magnesium has a brilliant metallic lustre, and a white colour like silver, is very malleable, and fuses at a red heat. Moist air oxidizes it superficially; but it undergoes no change in a dry air, and may be boiled in water without oxidation. Heated to redness in air or oxygen gas, it burns with brilliancy, yielding magnesia; and it inflames spontaneously in chlorine gas. It is readily dissolved by dilute acids with disengagement of hydrogen, and the solution is found to contain a pure salt of magnesia.

The equivalent of magnesium, inferred by Berzelius from the quantity of sulphate obtained from a known weight of pure magnesia, is 12.7. Its compounds described in this section are composed as follows:—

	Magnesium.				Equiv.	Formulæ.
Protoxide	12.7	1 eq.+Oxygen	8	1 eq.=	20.7	$Mg+O$ or $\dot{Mg}$.
Chloride	12.7	1 eq.+Chlorine	35.42	1 eq.=	48.12	$Mg+Cl$ or $MgCl$.
Iodide	12.7	1 eq.+Iodine	126.3	1 eq.=	139	$Mg+I$ or MgI.
Bromide	12.7	1 eq.+Bromine	78.4	1 eq.=	91.1	$Mg+Br$ or $MgBr$.
Fluoride	12.7	1 eq.+Fluorine	18.68	1 eq.=	31.38	Mg+MıF o gF.

Protoxide of Magnesium.—This, the only known oxide of magnesium, commonly known by the name of *magnesia*, is best obtained by exposing carbonate of magnesia to a very strong red heat, by which its carbonic acid is expelled. It is a white friable powder, of an earthy appearance; and, when pure, it has neither taste nor odour. Its specific gravity is about 2.3, and it is exceedingly infusible. It has a weaker affinity than lime for water; for though it forms a hydrate when moistened, the combination is effected with hardly any disengagement of caloric, and the product is readily decomposed by a red heat. There probably exist several different compounds of water and magnesia, but the native hydrate is the only one known with certainty. According to the analysis of Stromeyer, this hydrate contains one equivalent of each of its constituents; and the results of the analysis of Berzelius and Dr. Fyfe accord very nearly with this proportion.

Magnesia dissolves very sparingly in water. According to Dr. Fyfe, it requires 5142 times its weight of water at 60°, and 36,000 of boiling water for solution. The resulting liquid does not change the colour of violets; but when pure magnesia is put upon moistened turmeric paper, it causes a brown stain. From this there is no doubt that the inaction of magnesia with respect to vegetable colours, when tried in the ordinary mode, is owing to its insolubility. It possesses the still more essential character of akalinity, that, namely, of forming neutral salts with acids in an eminent degree. It absorbs both water and carbonic acid when exposed to the atmosphere, and, therefore, should be kept in well-closed phials.

Magnesia is characterized by the following properties. With nitric and hydrochloric acids it forms salts which are soluble in alcohol, and exceedingly deliquescent. The sulphate of magnesia is very soluble in water, a circumstance by which it is distinguished from the other alkaline earths. Magnesia is precipitated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of magnesia by the carbonates of potassa and soda; but the bicarbonates and the common carbonate of ammonia do not precipitate it in the cold. If moderately diluted, the salts of magnesia are not precipitated by oxalate of ammonia. By means of this reagent magnesia may be both distinguished and separated from lime.

Chloride.—This compound may be prepared by transmitting dry chlorine gas over a mixture of magnesia and charcoal at a red heat; but Liebig has given an easier process, which consists in dissolving magnesia in hydrochloric acid, evaporating to dryness, mixing the residue with its own weight of hydrochlorate of ammonia, and projecting the mixture in successive portions into a platinum crucible at a red heat. As soon as the ammoniacal salt is wholly expelled, the fused chloride of magnesium is left in a state of tranquil fusion, and on cooling becomes a transparent colourless mass, which is highly deliquescent, and is very soluble in alcohol and water.

Iodide of Magnesium is obtained by dissolving magnesia in hydriodic acid, is very soluble in water, and is only known in solution.

Bromide of Magnesium, obtained by dissolving magnesia in hydrobromic acid, crystallizes in small acicular prisms, which have a sharp taste, are deliquescent, and very soluble in water and alcohol. It is decomposed by a strong heat.

Fluoride of Magnesium is prepared by digesting magnesia in hydrofluoric acid in excess. It is insoluble in water and in excess of hydrofluoric acid, and bears a red heat without decomposition.

CLASS I.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION VIII.

ALUMINIUM.

That alumina is an oxidized body was proved by Sir H. Davy, who found that potassa is generated when the vapour of potassium is brought into contact with pure alumina heated to whiteness; and it was inferred, chiefly by analogical reasoning, to be a metallic oxide. The propriety of this inference has been demonstrated by Wöhler, who has procured *aluminium*, the metallic base of alumina, in a pure state. (Edinburgh Journal of Science, No. xvii. 178.)

The preparation of this metal depends on the property which potassium possesses of decomposing the chloride of aluminium. Decomposition is effected by aid of a moderate increase of temperature; but the action is so violent, and accompanied with such intense heat, that the process cannot be safely conducted in glass vessels. Wöhler succeeded with a platinum crucible, retaining the cover in its place by a piece of wire. The heat developed during the action was so great, that the crucible, though but gently heated externally, suddenly became red-hot. The platinum is scarcely attacked during the process; but to prevent the possibility of error from this source, the decomposition was also effected in a crucible of porcelain. The potassium employed for the purpose should be quite free from carbon, and the quantity operated on at one time not exceed the size of ten peas. The heat was applied by means of a spirit-lamp, and continued until the action was completed. The proportion of the materials requires to be carefully adjusted; for the potassium should be in such quantity as to prevent any chloride of aluminium from subliming during the process, but not so much as to yield an alkaline solution when the product is put into water. The matter, contained in the crucible at the close of the operation, is in general completely fused and of a dark gray colour. When *quite cold*, the crucible is put into a large glass full of water, in which the saline matter is dissolved, with slight disengagement of hydrogen of an offensive odour; and a gray powder separates, which, on close inspection, especially in sunshine, is found to consist solely of minute scales of metal. These scales, after being well washed with *cold* water, are pure aluminium. The saline matter removed by water is chloride of potassium, and a considerable quantity of chloride of aluminium.

Aluminium, as thus formed, is a gray powder, very similar to that of platinum. It is generally in small scales or spangles of a metallic lustre; and sometimes small, slightly coherent, spongy masses are observed, which in some places have the lustre and white colour of tin. The same appearance is rendered perfectly distinct by pressure on steel, or in an agate mortar; so that the lustre of aluminium is decidedly metallic. In its fused state it is a conductor of electricity, though it does not possess this property when in the form of powder. This remark, of a metal conducting the electric fluid in one state and not in another, is very instructive; and Wöhler observed an instance of the same kind in iron, which, in the state of fine powder, is a non-conductor of electricity.

Aluminium requires for fusion a temperature higher than that at which cast iron is liquefied. When heated to redness in the open air, it takes fire and burns with vivid light, yielding aluminous earth of a white colour and of considerable hardness. Sprinkled in powder in the flame of a candle, brilliant sparks are emitted, like those given off during the combustion of iron in oxygen gas. When heated to redness in a vessel of pure oxygen gas, it burns with an exceedingly vivid light, and emission of intense heat. The resulting alumina is partially vitrified, of a yellowish colour, and equal in hardness to the native crystallized aluminous earth, corundum. Heated to near redness in an atmosphere of chlorine, it takes fire, and chloride of aluminium is sublimed.

Aluminium is not oxidized by water at common temperatures, nor is its lustre tarnished by lying in water during its evaporation. On heating the water to near its boiling point, oxidation of the metal commences, with feeble disengagement of hydrogen gas, the evolution of which continues even long after cooling, but at length wholly ceases. The oxidation, however, is very slight; and even after continued ebullition, the smallest particles of aluminium appear to have suffered scarcely any change.

Aluminium is not attacked by concentrated sulphuric or nitric acid at common temperatures. In the former, with the aid of heat, it is rapidly dissolved with disengagement of sulphurous acid gas. In dilute hydrochloric and sulphuric acid, and also in a dilute solution of potassa, it dissolves with evolution of hydrogen gas. Ammonia produces a similar effect, and dissolves a large quantity of alumina. The hydrogen gas which makes its appearance is of course derived from water, the oxygen of which combines with the metal so as to constitute alumina.

From the composition of the sulphates of alumina, ascertained by Berzelius, Stromeyer, and Phillips, the equivalent of alumina may be estimated either at 25.7, or at 51.4, twice that number. Now chemists have no direct means of discovering the atomic constitution of alumina, inasmuch as aluminium combines with oxygen and most other elements in one proportion only. Thomson assumes alumina to consist of single atoms of its elements; but most chemists, seeing that alumina has little analogy to protoxides in its modes of combining, but that in its form and all its chemical relations it closely resembles peroxide of iron, have inferred that the simplest molecule of alumina contains two atoms of aluminium and three atoms of oxygen. On this supposition 51.4 must be the equivalent of alumina, and 13.7 that of aluminium. The composition of its compounds, described in this section, is the following:—

	2 eq. Aluminium.			Equiv.	Formulæ.
Sesquioxide	27.4 + oxygen	24	3 eq. =	51.4	$2Al + 3O$ or $\overset{\cdots}{\overline{Al}}$.
Sesquichloride	27.4 + chlorine	106.26	3 eq. =	133.66	$2Al + 3Cl$ or Al^2Cl^3
Sesquisulphuret	27.4 + sulphur	48.3	3 eq. =	75.7	$2Al + 3S$ or Al^2S^3.
Sesquiphosphuret	27.4 + phosph.	47.1	3 eq. =	74.5	$2Al + 3P$ or Al^2P^3.
Sesquiseleniuret	27.4 + selenium	118.8	3 eq. =	146.2	$2Al + 3Se$ or Al^2Se^3.

The composition of the four last compounds is matter of inference from the change which they respectively undergo by the action of water.

Sesquioxide of Aluminium.—This is the only known oxide of this metal, and is commonly known under the name of *alumina* or *aluminous earth.* It is one of the most abundant productions of nature. It is found in every region of the globe, and in rocks of all ages, being a constituent of the oldest primary mountains, of the secondary strata, and of the most recent alluvial depositions. The different kinds of clay of which bricks, pipes, and earthenware are made, consist of hydrate of alumina in a greater or less degree of purity. Though this earth commonly appears in rude amorphous masses, it is sometimes found beautifully crystallized.—The ruby and the sapphire, two of the most beautiful gems with which we are acquainted, are composed almost solely of alumina.

Pure alumina is prepared from alum, sulphate of alumina and potassa. This salt, as purchased in the shops, is frequently contaminated with peroxide of iron, and consequently unfit for many chemical purposes; but it may be separated from this impurity by repeated crystallization. Its absence is proved by the alum being soluble without residue in a solution of pure potassa; whereas when peroxide of iron is present, it is either left undissolved in the first instance, or deposited after a few hours in yellowish-brown flocks. Any quantity of purified alum is dissolved in four or five times its weight of boiling water, a slight excess of carbonate of potassa added, and after digesting for a few minutes, the bulky hydrate of alumina is collected on a filter, and well washed with hot water. It is necessary in this operation to digest and employ an excess of alkali; since otherwise the precipitate would retain some sulphuric acid in the form of a subsulphate. But the alumina, as thus prepared, is not yet quite pure; for it retains some of the alkali with such force, that it cannot be separated by the action of water. For this reason the precipitate must be re-dissolved in dilute hydrochloric acid, and thrown down by means of pure ammonia, or its carbonate. This precipitate, after being well washed and exposed to a white heat, yields pure anhydrous alumina. Ammonia cannot be employed for precipitating aluminous earth directly from alum, because sulphate of alumina is not completely decomposed by this alkali. (Berzelius.) An easier process, proposed by Gay-Lussac, is to expose sulphate of alumina and ammonia to a strong heat, so as to expel the ammonia and sulphuric acid.

Alumina has neither taste nor smell, and is quite insoluble in water. It is very infusible, though less so than lime or magnesia. It has a powerful affinity for water, attracting moisture from the atmosphere with avidity; and for a like reason, it adheres tenaciously to the tongue when applied to it. Mixed with a due proportion of water, it yields a soft cohesive mass, susceptible of being moulded into regular forms, a property upon which depends its employment in the art of pottery. When once moistened, it cannot be rendered anhydrous, except by exposure to a full white heat; and in proportion as it parts with water, its volume diminishes. (Page 27.)

Alumina, owing to its insolubility, does not affect the blue colour of plants. It appears to possess the properties both of an acid and of an alkali:—of an acid, by uniting with alkaline bases, such as potassa, lime, and baryta;—and of an alkali, by forming salts with acids. In neither case, however, are its soluble compounds neutral with respect to test paper.

Alumina most probably forms several different hydrates with water, and two have been described by Dr. Thomson. One of these, apparently composed of six equivalents of water to one of alumina, so that its formula is $\overset{\cdots}{\underline{Al}}+6\dot{H}$, was procured by exposing precipitated alumina for the space of two months to a dry air, the temperature of which did not exceed 60° F. The other is a terhydrate prepared by drying the preceding at a heat of about 100°, and its formula is, therefore, $\overset{\cdots}{\underline{Al}}+3\dot{H}$. The mineral called Gibbsite has a similar composition.

Alumina is easily recognized by the following characters. 1. It is separated from acids, as a hydrate, by all the alkaline carbonates, and by pure ammonia. 2. It is precipitated by pure potassa or soda, but the precipitate is completely redissolved by an excess of the alkali.

Sesquichloride of Aluminium.—Oersted discovered this compound by transmitting dry chlorine gas over a mixture of alumina and charcoal heated to redness. By acting on this substance with an amalgam of potassium and expelling the mercury by heat, he obtained metallic matter, which he believed to be aluminium; but not having leisure to pursue the inquiry himself, he requested Wöhler to investigate the subject. Wöhler did not arrive at any satisfactory conclusion by the method suggested by Oersted; but met with complete success by means of pure potassium, as already described.

To procure chloride of aluminium, Wöhler precipitated aluminous earth from a hot solution of alum by means of potassa, and mixed the hydrate, when dry, with pulverized charcoal, sugar, and oil, so as to form a thick paste, which was heated in a covered crucible until all the organic matter was destroyed. By this means the alumina was brought into a state of intimate mixture with finely divided charcoal, and while yet hot, was introduced into a tube of porcelain, fixed in a convenient furnace. After expelling atmospheric air from the interior of the apparatus by a current of dry chlorine gas, the tube was brought to a red heat. The formation of chloride of aluminium then commenced, and continued, with disengagement of carbonic oxide gas, during an hour and a half, when the tube became impervious from sublimed chloride of aluminium collected within it. The process was then necessarily discontinued.

As thus formed, chloride of aluminium is of a pale greenish-yellow colour, partially translucent, and of a highly crystalline lamellated texture, somewhat like talc, but without regular crystals. On exposure to the air it fumes slightly, emits an odour of hydrochloric acid gas, and, deliquescing, yields a clear liquid. When thrown into water, it is speedily dissolved with a hissing noise; and so much heat is evolved, that the water, if in small quantity, is brought into a state of brisk ebullition. The solution is probably a true hydrochlorate of alumina, formed by decomposition of water. According to Oersted it is volatile at a temperature a little higher than 212°, and fuses nearly at the same degree.

Sesquisulphuret of Aluminium.—Sulphur may be distilled from aluminium without combining with it; but if a piece of sulphur is dropped on aluminium when strongly incandescent, so that it may be enveloped in an atmosphere of the vapour of sulphur, the union is effected with vivid emission of light. The resulting sulphuret is a partially vitrified, semi-metallic mass, which acquires an iron-black metallic lustre when burnished. Applied to the tongue it excites a pricking warm taste of hydrosulphuric acid. When put into pure water, or on exposure to the air, it is resolved, by an interchange of elements, into alumina and hydrosulphuric acid, the latter escaping as gas. It is to be presumed that

1 eq. sulphuret and 3 eq. water yield 1 eq. alumina and 3 eq. hydrosulph. acid.
$2Al+3S$ $3(H+O)$ $2A+3O$ $3(H+S)$.

Wöhler finds that sulphuret of aluminium cannot be generated by the action of hydrogen gas on sulphate of alumina at a red heat; for in that case all the acid is expelled, without the aluminous earth being reduced.

Sesquiphosphuret of Aluminium.—When aluminium is heated to redness in contact with the vapour of phosphorus, it takes fire and emits a brilliant light. The product is described by Wöhler as a blackish-gray pulverulent mass, which by friction acquires a dark gray metallic lustre, and in the air smells instantly of phosphuretted hydrogen. By the action of water alumina and phosphuretted hydrogen gas are generated, but the latter is not spontaneously inflammable. The effervescence is less rapid than with the sulphuret, but is increased by heat.

Sesquiseleniuret of Aluminium.—This compound is formed, with disengagement of heat and light, by heating to redness a mixture of selenium and aluminium. The product is black and pulverulent, and assumes a dark metallic lustre when rubbed. In the air it emits a strong odour of hydroselenic acid; and this gas is rapidly disengaged by the action of water, which is speedily reddened by the separation of selenium.

SECTION IX.

GLUCINIUM, YTTRIUM, THORIUM, AND ZIRCONIUM.

GLUCINIUM.

Glucina, which was discovered by Vauquelin in the year 1798, has hitherto been found only in three rare minerals, the euclase, beryl, and emerald. It is the only oxide of a metal which Wöhler succeeded in preparing in the year 1828 by a process exactly similar to that described in the last section. Chloride of glucinium is readily attacked by potassium when heated with the flame of a spirit-lamp, and the decomposition is attended with intense heat. After removing the resulting chloride of potassium by cold water, the glucinium appears in the form of a grayish-black powder, which acquires a dark metallic lustre by burnishing. It may be exposed to air and moisture, or be even boiled in water, without oxidation. When heated in the open air, it takes fire and burns with a most vivid light; and in oxygen gas the combustion is attended with extraordinary splendour. The product in both cases is glucina, which is not at all fused by the intense heat that accompanied its formation. The metal is readily oxidized and dissolved in sulphuric, nitric, or hydrochloric acid with the aid of heat; and the same ensues, with disengagement of hydrogen gas, in solution of potassa. It is not attacked, however, by pure ammonia. When moderately heated in chlorine gas, it burns with great splendour, and a crystallized chloride sublimes. Similar phenomena ensue in the vapour of bromine and iodine; and it unites readily with sulphur, selenium, phosphorus, and arsenic. (Phil. Mag. and Annals, v. 392.)

According to the experiments of Berzelius, 25.7 is the equivalent of glucina; and, therefore, assuming it to consist of single equivalents, a point not yet clearly ascertained, the equivalent of glucinium is 17.7. Hence glucina will be formed of 17.7 parts or one eq. of glucinium and 8 parts or one eq. of oxygen.

Oxide of Glucinium or Glucina.—This oxide is commonly prepared from beryl, in which it exists to the extent of about 14 per cent., combined with silicic acid and alumina. In order to procure it in a separate state, the mineral is reduced to an exceedingly fine powder, mixed with three times its weight of carbonate of potassa, and exposed to a strong red heat for half an hour, so that the mixture may be fused. The mass is then dissolved in dilute hydrochloric acid, and the solution evaporated to perfect dryness; by which means the silicic acid is rendered quite insoluble. The alumina and glucina are then redissolved in water acidulated with hydrochloric acid, and thrown down together by pure ammonia. The precipitate, after being well washed, is macerated with a large excess of carbonate of ammonia, by which glucina is dissolved; and on boiling the filtered liquid, carbonate of glucina subsides. By means of a red heat its carbonic acid is entirely expelled.

Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its specific gravity is 3. Vegetable colours are not affected by it. The salts which it forms with acids have a sweetish taste, a circumstance which distinguishes glucina from other earths, and from which its name is derived. (From γλυκὺς, sweet.)

Glucina may be known chemically by the following characters. 1. Pure potassa or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as a hydrate, and by fixed alkaline carbonates as a carbonate of glucina. 3. It is dissolved completely by a cold solution of carbonate of ammonia, and is precipitated from it by boiling. By means of this property, glucina may be both distinguished and separated from alumina.

YTTRIUM.

Yttrium is the metallic base of an earth which was discovered in the year 1794 by Professor Gadolin, in a mineral found at Ytterby in Sweden, from which it received the name of *yttria*. The metal itself was prepared by Wöhler in 1828 by a process similar to that above described. Its texture, by which it is distinguished from glucinium and aluminium, is scaly, its colour grayish-black, and its lustre perfectly metallic. In colour and lustre it is inferior to aluminium, bearing in these respects nearly the same relation to that metal, that iron does to tin. It is a brittle metal, while aluminium is ductile. It is not oxidized either in air or water; but when heated to redness, it burns with splendour even in atmospheric air, and with far greater brilliancy in oxygen gas. The product, yttria, is white, and shows unequivocal marks of fusion. It dissolves in sulphuric acid, and also, though less readily, in solution of potassa; but it is not attacked by ammonia. It combines with sulphur, selenium, and phosphorus. (Phil. Mag. and Annals, v. 393.)

The salts of yttria have in general a sweet taste, and the sulphate, as well as many of its salts, has an amethyst colour. It is precipitated as a hydrate by the pure alkalies, and it is not redissolved by an excess of the precipitant; but alkaline carbonates, especially that of ammonia, dissolve it in the cold, though less freely than glucina, and carbonate of yttria is precipitated by boiling. Of all the earths it bears the closest resemblance to glucina; but

It is readily distinguished from it by the colour of its sulphate, by its insolubility in pure potassa, and by yielding a precipitate with ferrocyanuret of potassium. (Berzelius.) The equivalent of yttrium, as deduced by Berzelius, is 32.2; and that of yttria, which is probably a protoxide, is 40.2.

THORIUM.

The earthy substance formerly called *thorina*, was found by Berzelius to be phosphate of yttria; but in 1828 he discovered a new earth, so similar in some respects to what was formerly called thorina, that he applied this term to the new substance. Thorina was procured from a rare Norwegian mineral, now called *thorite*, which was sent to Berzelius by M. Esmarck. It constitutes 57.91 per cent. of the mineral, and occurs in the form of a hydrated silicate of thorina. In order to prepare thorina, the mineral is reduced to powder, and digested in hydrochloric acid; when a gelatinous mass is formed, from which silicic acid is separated by evaporating to dryness, and dissolving the soluble parts in dilute acid. The solution is then freed from lead and tin, which occur in thorite along with several impurities, by hydrosulphuric acid, and the earths are thrown down by pure ammonia. The precipitate, after being well washed, is dissolved in dilute sulphuric acid, and the solution evaporated at a high temperature till only a small quantity of fluid remains. During the evaporation the greater part of the thorina is deposited as a sulphate; and on decanting the remaining fluid, washing the residue, and heating it to redness, pure thorina remains. (An. de Ch. et de Ph. xliii. 5.)

The metallic base of thorina (thorium) was procured by the action of potassium on chloride of thorium, decomposition being accompanied with a slight detonation. On washing the mass, thorium is left in the form of a heavy metallic powder, of a deep leaden-gray colour; and when pressed in an agate mortar, it acquires metallic lustre and an iron-gray tint. Thorium is not oxidized either by hot or cold water; but when gently heated in the open air, it burns with great brilliancy, comparable to that of phosphorus burning in oxygen. The resulting thorina is as white as snow, and does not exhibit the least trace of fusion. It is not attacked by caustic alkalies at a boiling heat, is scarcely at all acted on by nitric acid, and very slowly by the sulphuric; but it is readily dissolved with disengagement of hydrogen gas by hydrochloric acid.

Thorina, when formed by the oxidation of thorium, or after being strongly heated, is a white earthy substance, of specific gravity 9.402, and insoluble in all the acids except the sulphuric; and it dissolves even in that with difficulty. It is precipitated from its solutions by the caustic alkalies as a hydrate, and in this state absorbs carbonic acid from the atmosphere, and dissolves readily in acids. All the alkaline carbonates dissolve the hydrate, carbonate, and sub-salts of thorina. Its exact composition is not known; but its equivalent is about 67.6.

Thorina is distinguished from alumina and glucina by its insolubility in pure potassa; from yttria by forming with sulphate of potassa a double salt which is quite insoluble in a cold saturated solution of sulphate of potassa; and from zirconia by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the acids. Thorina is precipitated, also, by ferrocyanuret of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling recovers its transparency.

Chloride of thorium is readily prepared by carbonizing an intimate mixture of thorina and sugar in a covered platinum crucible, and then exposing the residue at a red heat in a porcelain tube to a current of dry chlorine. The chloride, possessing but little volatility, collects in the tube just beyond the ignited part, in the form of a partially fused, crystalline, white mass. It is soluble in water with considerable rise of temperature.

When thorium is heated in the vapour of sulphur, the phenomena of combustion ensue with the same brilliancy as in air, and a sulphuret results. A phosphuret may be formed by a similar process.

ZIRCONIUM.

The experiments of Davy proved zirconia to be an oxidized body, and afforded a presumption that its base, *zirconium*, is of a metallic nature; but Berzelius first obtained the metal in 1824, by heating, with a spirit-lamp, a mixture of potassium and the double fluoride of zirconium and potassium, carefully dried, in a tube of glass or iron. The reduction takes place at a temperature below redness, without emission of light; and the mass is washed with boiling water, and afterwards digested for some time in dilute hydrochloric acid. The residue is pure zirconium.

Zirconium, thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by sulphuric, hydrochloric, or nitro-hydrochloric acid; but it is dissolved readily, and with disengagement of hydrogen gas, by hydrofluoric acid. Heated in the open air, it takes fire at a temperature far below luminousness, burns brightly, and is converted into zirconia. Its metallic nature seems somewhat questionable. It may indeed be pressed out into thin shining scales of a dark gray colour, and of a lustre which may be called metallic; but its particles cohere together very feebly, and it has not been procured in a state capable of conducting electricity. These points, however, require further investigation before a decisive opinion on the subject can be adopted. (Pog. Annalen, iv.)

Oxide of Zirconium was discovered in the year 1789 by Klaproth in the jargon or zircon of Ceylon, and has since been found in the hyacinth from Expailly in France. It is an earthy substance, resembling alumina in appearance, of specific gravity 4.3, having neither taste nor odour, and quite insoluble in water. It is so hard that it will scratch glass. Its colour, when pure, is white; but it has frequently a tinge of yellow, owing to the presence of iron, from which it is separated with great difficulty. It phosphoresces vividly when heated strongly before the blowpipe. Its salts are distinguished from those of alumina or glucina by being precipitated by all the pure alkalies, in an excess of which it is insoluble. The alkaline carbonates precipitate it as carbonate of zirconia, and a small portion of it is redissolved by an excess of the precipitant, especially when a bicarbonate is employed. It differs from all the earths, except thorina, in being precipitated when any of its neutral salts are boiled with a saturated solution of sulphate of potassa, the zirconia subsiding as a subsalt, and the potassa remaining in solution as a bisulphate. Zirconia is precipitated from its salts by pure ammonia as a bulky hydrate, which is readily soluble in acids; but if this hydrate is ignited, dried, or even washed with boiling water, it afterwards resists the action of the acids, and is dissolved by them with great difficulty. Strong sulphuric acid is then its best solvent. (Berzelius.) When hydrated zirconia is heated to commencing redness, it parts with its water, and soon after emits a very vivid glow for a short time. This phenomenon appears to depend upon the particles of the zirconia suddenly approaching each other, and thus acquiring much greater density than it previously possessed. Oxide of chromium, titanic acid, and several other compounds, afford instances of the same appearance; and whenever it takes place, the susceptibility of the substance to be attacked by fluid reagents is greatly diminished. (Berzelius.)

The composition of zirconia has not yet been satisfactorily determined.

From some analyses by Berzelius, described in the Essay above referred to, it is probable that the atomic weight of this earth is about 30 or 33.*

Sulphuret of Zirconium.—This compound may be prepared, according to Berzelius, by heating zirconium with sulphur in an atmosphere of hydrogen gas; and the union is effected with feeble emission of light. The product is pulverulent, a non-conductor of electricity, of a dark chestnut-brown colour, and without lustre. It is insoluble in sulphuric, nitric, and hydrochloric acid; and it is slowly attacked by nitro-hydrochloric acid, even with the aid of heat. It is readily dissolved by hydrofluoric acid, with disengagement of hydrogen gas.

SECTION X.

SILICIUM.

That silicic acid or silica is composed of a combustible body united with oxygen, was demonstrated by Davy; for on bringing the vapour of potassium in contact with pure silicic acid heated to whiteness, a silicate of potassa resulted, through which was diffused the inflammable base of silicic acid in the form of black particles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silica, that Dr. Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it in his system of chemistry with carbon and boron under the name of *silicon*. The recent researches of Berzelius appear almost decisive of this question. A substance which wants the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal. It may not be improper, however, to have the absence of these qualities more completely ascertained, before separating silica from a class of bodies with which, in several respects, it is so nearly allied.

Pure silicium was first procured by Berzelius in the year 1824 by the action of potassium on fluosilicic acid gas; but it is more conveniently prepared from the double fluoride of silicium and potassium or sodium, previously dried by a temperature near that of redness. When this compound is heated in a glass tube with potassium, the latter unites with fluorine, and silicium is separated. The heat of a spirit-lamp is sufficient for the purpose, and the decomposition takes place, accompanied with feeble detonation, before the mixture becomes red-hot. When the mass is cold, the soluble parts are removed by the action of water; the first portions of which produce disengagement of hydrogen gas, owing to the presence of some siliciuret of potassium. The silicium thus procured is chemically united with a little hydrogen, and at a red heat burns vividly in oxygen gas. In order to render it quite pure, it should be first heated to redness, and then digested in dilute hydrofluoric acid to dissolve adherent particles of silicic acid. (Annals of Philosophy, xxvi. 116.)

Silicium obtained in this manner has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blowpipe without fusing or undergoing any other change. It is neither dissolved nor oxidized by the sulphuric, nitric, hydrochloric, or hydrofluoric acid; but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold.*

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* Dr. Turner here no doubt intended to say that the atomic weight of *zirconium* is 30 or 33. Berzelius makes the atomic weight of this radical 33.671, which is nearly the same number with that given by Dr. Turner for zirconium in the table of equivalents at page 141.—*Ed.*

Silicium is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silicic acid, co-operating with the attraction of oxygen for silicium. For a similar reason it burns vividly when brought into contact with carbonate of potassa or soda, and the combustion ensues at a temperature considerably below that of redness. It explodes in consequence of a copious evolution of hydrogen gas, when it is dropped upon the fused hydrate of potassa, soda, or baryta.

Berzelius ascertained, by oxidizing a known weight of silicium, that 100 parts of silicic acid are composed of 48.4 of silicium and 51.6 of oxygen. Now if silicic acid, as Dr. Thomson supposes, be composed of single atoms of its elements, then the equivalent of silicium will be 7.5; but if, as Berzelius believes, the smallest molecule of that acid contain three atoms of oxygen united with one atom of silicium, the equivalent of silicium would be 22.5. The latter view is supported by very strong analogies; but as the former applies more conveniently in expressing the composition of the silicates, I have adopted it by preference. The composition of the compounds of silicium, described in this section, may accordingly be stated as follows:—

	Silicium.			Equiv.	Formulæ.
Silicic acid . .	7.5	1 eq.+Oxygen	8	1 eq.=15.5	Si+O or $\dot{Si}$.
Chloride . . .	7.5	1 eq+.Chlorine	35.42	1 eq.=42.92	Si+Cl or SiCl.
Bromide . . .	7.5	1 eq.+Bromine	78.4	1 eq.=85.9	Si+Br or SiBr.
Sulphuret . . .	7.5	1 eq.+Sulphur	16.1	1 eq.=23.6	Si+S or SiS.
Fluosilicic acid gas	7.5	1 eq.+Fluorine	18.68	1 eq.=26.18	Si+F or SiF.

Silicic Acid.—This compound, known also by the names of *silica* and *siliceous earth*, exists abundantly in nature. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient of sandstones, flint, calcedony, rock crystal, and other analogous substances. It may indeed be procured, of sufficient purity for most purposes, by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

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* Dr. Turner has not, perhaps, described with sufficient distinctness, the two states under which silicium appears. Its characters are so much altered by exposure to a high temperature, that Berzelius has deemed it expedient to give a separate description of its properties, as it appears before and after ignition.

Silicium before ignition is neither oxidized nor dissolved by sulphuric, nitric, or nitro-muriatic acid, even at the boiling temperature; but it is soluble in liquid hydrofluoric acid at common temperatures, and in a heated concentrated solution of caustic potassa. It burns readily and vividly in air, and still more vividly in oxygen gas. A part of it only undergoes combustion, the remainder being protected by the coating of silica which becomes formed. In this state silicium contains a little hydrogen.

If a portion of silicium which has undergone combustion on its surface, be subjected to the action of hydrofluoric acid, the silica is removed, and a nucleus of silicium is obtained in that state in which it exists, after having been condensed and altered in its properties by heat. It is now perfectly incombustible, and is no longer soluble in hydrofluoric acid or a solution of caustic potassa.

Berzelius does not appear to attribute the difference in properties between the two forms of silicium to the presence of hydrogen in one of them; but rather to a difference in the aggregation of the particles. *Berzelius, Traité de Chimie*, i. 370.—*Ed.*

Pure sillicic acid, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers, and is both insipid and inodorous. It is fixed in the fire, and very infusible; but fuses before the oxy-hydrogen blowpipe with greater facility than lime or magnesia.

In its solid form silicic acid is quite insoluble in water; but Berzelius has shown, that if presented to water while in the nascent state, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous hydrate separates, which is partially decomposed by a very moderate temperature, but does not part with all its water except at a red heat.

Silicic acid has no action on test paper; but in all its chemical relations it manifests the properties of an acid, and displaces carbonic acid by the aid of heat from the alkalies. Its combinations with the fixed alkalies are effected by mixing pure sand with carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silicic acid with three of carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silicic acid as a gelatinous hydrate; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silicic acid. When a solution of this kind is evaporated to dryness, the silicic acid is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silicic acid and alkali be reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the hydrofluoric, and possesses the well-known properties of glass. Every kind of ordinary glass is a silicate, and all its varieties are owing to differences in the proportion of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus, green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearl ashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking-glasses, is composed of sand and alkali in their purest state; and in the formation of flint glass, besides these pure ingredients, a considerable quantity of litharge or red lead is employed. A small portion of peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass; and nitre is sometimes added with the same intention. Ordinary flint glass, according to Mr. Faraday, contains 51.93 per cent. of silicic acid, 33.28 of oxide of lead, and 13.77 of potassa; proportions which correspond to one eq. of potassa, one eq. of oxide of lead, and nearly twelve eq. of silicic acid. Flint glass, accordingly, is a double salt, consisting chiefly of sexsilicate of potassa and sexsilicate of oxide of lead.

Chloride of Silicium.—When silicium is heated in a current of chlorine gas, it takes fire, and is rapidly volatilized. The product of the combustion condenses into a liquid, which appears to be naturally colourless, but to which an excess of chlorine communicates a yellow tint. This fluid is very limpid and volatile, and evaporates almost instantaneously in open vessels in the form of a white vapour. It boils at 124°, and bears a cold of zero without becoming solid. It has a suffocating odour not unlike that of cyanogen, and when put into water is converted into hydrochloric and silicic acids, the latter being easily obtained in a gelatinous form. (Berzelius.)

This chloride may also be prepared by the method proposed by Oersted, which has been so successfully applied in the formation of other chlorides. It consists in mixing about equal parts of hydrated silicic acid and starch into a paste with oil, heating the mass in a covered crucible so as to char the starch, introducing the mixture in fragments into a porcelain tube, and then transmitting through it a current of dry chlorine gas, while the tube is kept at a red heat. The chlorine unites with silicium, while the charcoal and oxygen combine. The volatile chloride is then agitated with mercury to separate the free chlorine, and purified by distillation.

Bromide of Silicium.—This compound was made by Serullas in precisely the same mode as that just described, merely substituting the vapour of bromine for chlorine. When purified from free bromine by mercury, and redistilled, it is a colourless liquid, which emits dense vapours in an open vessel, being decomposed by the moisture of the air, and is denser than strong sulphuric acid. At 302° it enters into ebullition, and freezes at 10°. Potassium, when gently heated, acts on it with such energy that detonation ensues. By water it is resolved into hydrobromic and silicic acids. (Phil. Mag. and Annals, xi. 395.)

Sulphuret of Silicium.—This compound is formed by heating silicium in the vapour of sulphur, and the union is attended with the phenomena of combustion. The product is a white earthy-looking substance, which is instantly converted by the action of water into hydrosulphuric and silicic acids; and while the former escapes with effervescence, the latter is dissolved in large quantity. In open vessels, owing to the moisture of the atmosphere, it undergoes a similar change; but in dry air it may be kept unaltered.

Fluosilicic Acid.—This gas is formed whenever hydrofluoric and silicic acids come in contact; and hence pure hydrofluoric acid can be prepared in metallic vessels only, and with fluor spar that is free from rock crystal. The most convenient method of procuring it, is to mix in a retort one part of pulverized fluor spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

The chemical changes attending this process are differently explained, according to the view which is taken concerning the nature of the product. In regarding fluor spar as a compound of fluoric acid and lime, the former at the moment of being set free is thought to unite directly with silicic acid, thereby giving rise to a compound of silicic and fluoric acids. But for reasons already stated (page 240), fluor spar is not considered as fluate of lime; and, therefore, this view cannot be admitted. It is inferred, on the contrary, that when, by the action of sulphuric acid on fluoride of calcium, hydrofluoric acid is generated, the elements of this acid react on those of silicic acid, and give rise to the production of water and fluosilicic acid gas. This gas is, therefore, a fluoride of silicium. It may occur to some whether hydrofluoric acid does not unite directly with silicic acid; but this idea is inconsistent with the proportion in which the elements of the gas are found to be united.

This compound is a colourless gas which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air it forms a white cloud, owing to the presence of watery vapour. Its specific gravity, according to Dr. Thomson, is 3.6111; and 100 cubic inches of it at 60°, and when the barometer stands at 30 inches, weigh 111.986 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr. Davy, 365 times its volume. (Philos. Trans. for 1812.) The gas suffers decomposition at the moment of contact with water, silicic acid in the form of a gelatinous hydrate being deposited, which when well washed is quite pure. The liquid, which has a sour taste and reddens litmus paper, contains the whole of the hydrofluoric acid, together with two-thirds of the silicic acid which was originally present in the gas. (Berzelius.) By conducting fluosilicic acid gas into a solution of ammonia, complete decomposition ensues:—hydrofluoric acid unites with the alkali, forming hydrofluate of ammonia, and all the silicic acid is deposited. On this fact is founded the mode of analyzing fluosilicic acid gas, adopted by Dr. Davy and Dr. Thomson.

The solution which is formed by fully saturating water with fluosilicic acid gas is powerfully acid, and emits fumes on exposure to the air. It is commonly known by the name of *silicated fluoric acid;* but a more appropriate term is *silico-hydrofluoric acid.* According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric and silicic acids, in the ratio of three equivalents of the former to two of the latter. If evaporated before separation from the silicic acid, deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silicic acid thus deposited, and then evaporated, fluosilicic acid gas is at first evolved, and subsequently hydrofluoric acid and water are expelled. The evaporation of silico-hydrofluoric acid *in vacuo* is attended by a similar change, so that this acid cannot be obtained free from water. It does not corrode glass; but when evaporated in glass vessels, the production of free hydrofluoric acid of course gives rise to corrosion.

On neutralizing silico-hydrofluoric acid with ammonia, and gently evaporating to dryness, all the silicic acid is rendered insoluble. By exactly neutralizing with carbonate of potassa, a sparingly soluble double fluoride of silicium and potassium subsides. The precipitation is still more complete with chloride of barium, when the insoluble fluoride of silicium and barium is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silico-hydrofluoric acid on metallic oxides.

CLASS II.

METALS, THE OXIDES OF WHICH ARE NEITHER ALKALIES NOR EARTHS.

ORDER I.

METALS WHICH DECOMPOSE WATER AT A RED HEAT.

SECTION XI.

MANGANESE.

The black oxide of manganese was described in the year 1774 by Scheele as a peculiar earth, and Gahn subsequently showed that it contains a new metal, to which he gave the name of *magnesium;* a term since applied to the metallic base of magnesia, and for which the words *manganesium* and *manganium* have been substituted. This metal, owing doubtless to its strong affinity for oxygen, has never been found in an uncombined state in the earth; but its oxides are very abundant. The metal may be obtained by forming finely powdered oxide of manganese into a paste with oil, laying the mass in a Hessian crucible lined with charcoal, luting down a cover carefully, and exposing it during an hour and a half, or two hours, to the strongest heat of a smith's forge.

Manganese is a hard brittle metal, of a grayish-white colour, and granular texture. Its specific gravity, according to John, is 8.013. When pure it is not attracted by the magnet. It is exceedingly infusible, requiring the highest heat of a wind furnace for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. It slowly decomposes water at common temperatures with disengagement of hydrogen gas; but at a red heat decomposition is rapid, and protoxide of manganese is generated. Decomposition of water is likewise occasioned by dilute sulphuric acid, and sulphate of protoxide of manganese is the product.

Berzelius, from an analysis of chloride of manganese, found 27.7 as the equivalent of manganese, a number which agrees closely with my own experiments on the same chloride. The composition of the compounds of manganese described in this section is as follows:—

Manganese.					Equiv.	Formulæ.
Protoxide	27.7	1 eq. + Oxygen	8	1 eq.=	35.7	Mn + O or $\dot{\mathrm{Mn}}$.
Sesquioxide	55.4	2 eq. + do.	24	3 eq.=	79.4	2Mn + 3O or $\underline{\dddot{\mathrm{Mn}}}$.
Peroxide	27.7	1 eq. + do.	16	2 eq.=	43.7	Mn + 2O or $\ddot{\mathrm{Mn}}$.
Red Oxide	83.1	3 eq. + do.	32	4 eq.=	115.1	3Mn + 4O or Mn^3O^4.
Varvicite	110.8	4 eq. + do.	56	7 eq.=	166.8	4Mn + 7O or Mn^4O_7.
Manganic acid	27.7	1 eq. + do.	24	3 eq.=	51.7	Mn + 3O or $\dddot{\mathrm{Mn}}$.
Perman. acid	55.4	2 eq. + do.	56	7 eq.=	111.4	2Mn + 7O or $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{Mn}}}$.
Protochloride	27.7	1 eq. + Chlor.	35.42	1 eq.=	63.12	Mn + Cl or MnCl.
Perchloride.	55.4	2 eq. + do.	247.94	7 eq.=	303.34	2Mn + 7Cl or Mn^2Cl^7.
Perfluoride	55.4	2 eq. + Fluor.	130.76	7 eq.=	186.16	2Mn + 7F or Mn^2F_7.
Protosulphuret	27.7	1 eq. + Sulph.	16.1	1 eq.=	43.8	Mn + S or MnS.
Cyanuret	27.7	1 eq. + Cyano.	26.39	1 eq.=	54.09	Mn + Cy or MnCy.

OXIDES OF MANGANESE.

In studying metallic oxides, it is necessary to distinguish oxides formed by the direct union of oxygen and a metal, from those that consist of two other oxides united with each other, and which, therefore, in composition, partake of the nature of a salt rather than of an oxide. An instance of this kind of combination is supplied by the black oxide of iron; and it is probable that two, if not three, of the five compounds enumerated as oxides of manganese, have a similar constitution. Their composition has been particularly investigated by Berzelius, Dr. Thomson, (First Principles, i.) M. Arfwedson,* M. Berthier,† and myself.‡

Sesquioxide.—This oxide occurs nearly pure in nature, and as a hydrate it is found abundantly, often in large prismatic crystals, at Jhlefeld, in the Hartz. It may be formed artificially by exposing peroxide of manganese for a considerable time to a moderate red heat, and, therefore, is the chief residue of the usual process for procuring a supply of oxygen gas; but it is difficult so to regulate the degree and duration of the heat, that the resulting oxide shall be quite pure.

The colour of the sesquioxide of manganese varies with the source from which it is derived. That which is procured by means of heat from the native peroxide or hydrated sesquioxide has a brown tint; but when prepared from nitrate of oxide of manganese, it is nearly as black as the peroxide, and the native sesquioxide is of the same colour. With sulphuric and hydrochloric acids, it gives rise to the same phenomenon as the peroxide, but of course yields a smaller proportional quantity of oxygen and chlorine gases. It is more easily attacked than the peroxide by cold sulphuric acid. With strong nitric acid, it yields a soluble protonitrate and the peroxide, as observed by Berthier; and when boiled with dilute sulphuric acid, it undergoes a similar change. From the proportion of oxygen and manganese in this oxide, it may be regarded as a compound of 43.7 parts or one equivalent of peroxide, and 35.7 parts or one equivalent of protoxide of manganese. In that case its formula would be $\dot{M}n+\ddot{M}n$.

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* Letter from Berzelius in the An. de Ch. et de Ph. vi. † Ibid. xx.
‡ Philos. Trans. of Edin. for 1828; or Phil. Mag. and Annals, iv.

Peroxide.—This is the well-known ore commonly called from its colour black oxide of manganese. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron, and carbonate of lime. It is sometimes found, on the contrary, in the form of minute prisms grouped together, and radiating from a common centre. In these states it is anhydrous; but the essential ingredient of one variety of the earthy mineral, called *wad*, is hydrated peroxide of manganese, consisting of one equivalent of water and two of the oxide. The peroxide may be made artificially by exposing nitrate of oxide of manganese to a commencing red heat, until the whole of the nitric acid is expelled; but I have never succeeded in procuring it quite pure by this process, because the heat required to drive off the last traces of acid, likewise expels some oxygen from the peroxide. The hydrated peroxide, containing one equivalent of water and one of oxide, is formed by precipitating the protochloride of manganese by chloride of lime; and the same compound results from the decomposition of the acids of manganese either in water or by dilute acid. For our knowledge of this hydrate we are indebted to Berthier.

Peroxide of manganese undergoes no change on exposure to the air. It is insoluble in water, and does not unite either with acids or alkalies. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed (page 153.) With hydrochloric acid, chloride of manganese is generated, and chlorine is evolved (page 209.) The solution in both cases is of a deep-red colour, provided undissolved oxide is present; but if separated from the undissolved portions, it is readily rendered colourless by heat. The colour is commonly attributed to a small quantity of the sesquioxide or red oxide of manganese dissolved by the free acid; but Mr. Pearsall of Hull has gone far to prove that it is owing to the presence of permanganic acid. (R. Inst. Journal, N.S. No. iv. 49.) The action of sulphuric acid in the cold is exceedingly tardy and feeble, a minute quantity of oxygen gas is slowly disengaged, and the acid acquires an amethyst-red tint, On exposure to a red heat, it is converted, with evolution of oxygen gas, into the sesquioxide of manganese. (Page 153.)

Peroxide of manganese is employed in the arts, in the manufacture of glass, and in preparing chlorine for bleaching. In the laboratory it is used for procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

Protoxide.—By this term is meant that oxide of manganese which is a strong salifiable base, is contained in all the ordinary salts of this metal, and which appears to be its lowest degree of oxidation. This oxide may be formed, as was shown by Berthier, by exposing the peroxide, sesquioxide, or red oxide of manganese to the combined agency of charcoal and a white heat; and Dr. Forchammer, in the Annals of Philosophy, xvii. 52, has described an elegant mode of preparation, by exposing either of the oxides of manganese contained in a tube of glass, porcelain, or iron, to a current of hydrogen gas at an elevated temperature. The best material for this purpose is the red oxide prepared from nitrate of oxide of manganese; since the native oxides, especially the peroxide, are fully reduced to the state of protoxide by hydrogen with difficulty. The reduction commences at a low red heat; but to decompose all the red oxide, a full red heat is required. The same compound is formed by the action of hydrogen gas at an intense white heat. Wöhler and Liebig have shown that the protoxide is also obtained by fusing chloride of manganese in a platinum crucible with about twice its weight of carbonate of soda, and afterwards dissolving the chloride of sodium by water.

Protoxide of manganese, when pure, is of a light green colour, very near the mountain green. According to Forchammer it attracts oxygen rapidly from the air; but in my experiments it was very permanent, undergoing no change either in weight or appearance during the space of nineteen days. At 600° it is oxidized with considerable rapidity, and at a low red heat is converted in an instant into red oxide. It sometimes takes fire when thus heated, especially when the mass is considerable. It unites readily with acids without effervescence, producing the same salts as when the same acids act on carbonate of oxide of manganese. When it comes in contact with concentrated sulphuric acid, intense heat is instantly evolved; and the same phenomenon is produced, though in a less degree, by strong hydrochloric acid.—The resulting salt is the same as when these acids are heated with either of the other oxides of manganese. If quite pure, the protoxide should readily and completely dissolve in cold dilute sulphuric acid, and yield a colourless solution.

In order to prepare a pure salt of manganese from the common peroxide of commerce, either of the following processes may be employed. The impure sesquioxide left in the process for procuring oxygen gas from the peroxide by heat, is mixed with a sixth of its weight of charcoal in powder, and exposed to a white heat for half an hour in a covered crucible. The protoxide thus formed is to be dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue kept for a quarter of an hour in perfect fusion; being protected as much as possible from the air. By this means the chlorides of iron, calcium, and other metals are decomposed.

The fused chloride of manganese is then poured out on a clean sandstone, dissolved in water, and the solution separated from insoluble matters by filtration. If free from iron, it will give a white precipitate with ferrocyanuret of potassium, without any appearance of green or blue, and a flesh-coloured precipitate with hydrosulphate of ammonia. The protoxide is thrown down as a white carbonate by bicarbonate of potassa or soda; and from this salt, after being well washed, all the other salts of manganese may be prepared. The other method of forming a pure chloride was suggested by Mr. Faraday, and consists in heating to redness a mixture of peroxide of manganese with half its weight of hydrochlorate of ammonia. Owing to the volatility of the sal ammoniac it is necessary to apply the required heat as rapidly as possible, and this is best done by projecting the mixture in small portions at a time into a crucible kept red-hot. In this process the chlorine of the hydrochloric acid unites with the metal of the oxide to the exclusion of every other substance, provided an excess of manganese be present. The resulting chloride is then dissolved in water, and the insoluble matters separated by filtration. (Faraday in Quart. Journal, vi.)

In preparing manganese of great purity, the operator should bear in mind that the precipitated carbonate sometimes contains hydrochloric acid. It may likewise contain traces of lime; for oxalate of lime, insoluble as it is in pure water, does not completely subside from a strong solution of chloride of manganese, and, therefore, a small quantity of that earth may be present, although not indicated by oxalate of ammonia.

The salts of manganese are in general colourless if quite pure; but more frequently they have a shade of pink, owing to the presence of a little red oxide or permanganic acid. The protoxide is precipitated from its solutions as a white hydrate by ammonia, or the pure fixed alkalies; as white carbonate of protoxide of manganese by alkaline carbonates and bicarbonates; and as white ferrocyanuret of manganese by ferrocyanuret of potassium, a character by which the absence of iron may be demonstrated. These white precipitates, with the exception of that obtained by means of a bicarbonate, very soon become brown from the absorption of oxygen. None of the salts of manganese which contain a strong acid, such as the nitric, or sulphuric, are precipitated by hydrosulphuric acid. With an alkaline hydrosulphate, on the contrary, a flesh-coloured precipitate is formed, which is a hydrated protosulphuret of manganese: when heated in close vessels, it yields a dark-coloured sulphuret, and water is evolved.

Red Oxide.—The substance called red oxide of manganese, *oxidum manganoso-manganicum* of Arfwedson, occurs as a natural production, and may be formed artificially by exposing the peroxide or sesquioxide to a white heat either in close or open vessels. It is also produced by absorption of oxygen from the atmosphere when the protoxide is precipitated from its salts by pure alkalies, or when the anhydrous protoxide or carbonate is heated to redness. It is very permanent in the air, not passing to a higher state of oxidation at any temperature. Its colour when rubbed to the same degree of fineness is brownish-red when cold, and nearly black while warm. Fused with borax or glass it communicates a beautiful violet tint, a character by which manganese may be easily detected before the blowpipe; and it is the cause of the rich colour of the amethyst. It is acted on by strong sulphuric and hydrochloric acids, with the aid of heat, in the same manner as the peroxide and sesquioxide, but of course yields proportionally a smaller quantity of oxygen and chlorine gases. By cold concentrated sulphuric acid it is dissolved in small quantity, without appreciable disengagement of oxygen gas, and the solution is promoted by a slight increase of temperature. The liquid has an amethyst tint, which disappears when heat is applied, or by the action of deoxidizing substances, such as protochloride of tin, or sulphurous and phosphorous acids, sulphate of protoxide of manganese being generated. By strong nitric acid, or when boiled with dilute sulphuric acid, it undergoes the same kind of change as the sesquioxide.

It may be doubted whether the red oxide is not rather a kind of salt composed of two other oxides, than a direct compound of manganese and oxygen. From the ratio of its elements it may consist either of

Sesquioxide	79.4 or one eq.	or	Peroxide	43.7 or one eq.
Protoxide	35.7 or one eq.		Protoxide	71.4 or two eq.
	115.1			115.1

It contains 27.586 per cent. of oxygen, and loses 6.896 per cent. when converted into the green oxide.

Varvicite.—This compound is known only as a natural production, having been first noticed a few years ago by Mr. Phillips among some ores of manganese found at Hartshill, in Warwickshire. The locality of the mineral suggested its name; but I have also detected it as the constituent of an ore of manganese from Jhlefeld, sent me by Professor Stromeyer. Varvicite was at first mistaken for peroxide of manganese, to which in the colour of its powder it bears considerable resemblance; but it is readily distinguished from that ore by its stronger lustre, greater hardness, more lamellated texture, which is very similar to that of manganite, and by yielding water freely when heated to redness. Its sp. gravity is 4.531. It has not been found regularly crystallized; but my specimen from Jhlefeld is in *pseudo-crystals*, possessing the form of the six-sided pyramid of calcareous spar. When strongly heated it is converted into red oxide, losing 5.725 per cent. of water, and 7.385 of oxygen. It is probably, like the red oxide, a compound of two other oxides; and the proportions just stated justify the supposition that it consists of two equivalents of peroxide and one of sesquioxide of manganese, united in the mineral with an equivalent of water. (Phil. Mag. and Annals, v. 209, vi. 281, and vii. 284.)

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese, which contain less oxygen than the green or protoxide. We have no proof, however, of the existence of such compounds.

Manganic Acid.—Manganese is one of those metals which is capable of forming an acid with oxygen. Manganate of potassa is generated when hydrate or carbonate of potassa is heated to redness with peroxide of manganese; and nitre may be used successfully, provided the heat be high enough to decompose the nitrate of potassa. The materials absorb oxygen from the air when fused in open vessels; but manganate of potassa is equally well formed in close vessels, one portion of oxide of manganese then supplying oxygen to another. The product has been long known under the name of ***mineral chameleon***, from the property of its solution to pass rapidly through several shades of colour: on the first addition of cold water, a green solution is formed which soon becomes blue, purple, and red; and ultimately a brown flocculent matter, hydrated peroxide of manganese, subsides, and the liquid becomes colourless. These changes, which are more rapid by dilution and with hot water, have been successively elucidated by Chevillot and Edwards, Forchammer, and Mitscherlich. (An. de Ch. et de Ph. viii, and xlix. 113, and An. of Phil. xvi.)

The phenomena above mentioned are owing to the formation of manganate of potassa of a green colour, and to its ready conversion into the red permanganate of potassa, the blue and purple tints being due to a mixture of these compounds. Manganic acid itself cannot be obtained in an uncombined state, because it is then resolved into the hydrated peroxide and oxygen, a property which Mitscherlich availed himself of in analyzing this acid; but Mitscherlich has proved that it is analogous in composition to sulphuric acid, and its salts isomorphous with the sulphates. Manganate of potassa is obtained in crystals by forming a concentrated solution of mineral chameleon in cold water, very pure and free from carbonic acid, allowing it to subside in a stoppered bottle, and evaporating the clear green solution in vacuo with the aid of sulphuric acid. All contact of paper and other organic matter must be carefully avoided, since they deoxidize the acid, and the process be conducted in a cool apartment. The crystals are anhydrous, and permanent in the dry state; but in solution the carbonic acid of the air suffices to decompose the acid, or even simple dilution with cold water. Mixed with a solution of potassa, the manganate may be crystallized a second time in vacuo without change.

Permanganic Acid.—This acid is more stable than the manganic, though itself very prone to decomposition. Contact with paper or linen as in filtering, particles of cork, organic particles floating in the atmosphere decompose it rapidly; colouring matters are bleached by it; and in pure water its decomposition begins at 86°, and is complete at 212°. On these occasions oxygen gas is abstracted or given out, and hydrated peroxide of manganese subsides. The acid has a rich red colour, and is obtained by adding to a solution of permanganate of baryta, a quantity of dilute sulphuric acid exactly sufficient for precipitating the baryta.

The salts of permanganic acid are more permanent than the free acid; so that most of them may be boiled in solution, especially if concentrated. Permanganate of potassa is obtained by heating a green solution of mineral chameleon however prepared; but a very good process has been indicated by Wöhler. (Pog. Annalen, xxvii. 626.) It consists in fusing chlorate of potassa in a platinum crucible, introducing a few fragments of hydrate of potassa, and then adding peroxide of manganese in fine powder. Manganate of potassa is instantly formed; and after decomposing any excess of chlorate of potassa by a red heat, the soluble parts are taken up in pure water, the manganate converted by boiling into permanganate of potassa, and the hot solution, decanted from the insoluble oxide of manganese, is set aside to crystallize. As the permanganate is much less soluble than the chloride of potassium in cold water, the former separates in opaque prismatic crystals, and the latter is left in solution. These crystals have so intense a colour that they appear black, and have a lustre like bronze; but their powder has a purple-red tint. They are permanent at common temperatures; but when heated give out oxygen gas, and are reconverted into manganate of potassa. They deflagrate like nitre with burning charcoal, and detonate powerfully with phosphorus. Their colour in solution is a rich purple, and a small quantity of the salt imparts this colour to a very large quantity of water. When mixed with dilute nitric acid and boiled, oxygen gas is evolved, and hydrated peroxide of manganese subsides, from the respective quantities of which Mitscherlich ascertained the composition of the acid. In addition to the remarkable analogy which its constitution bears to perchloric acid, Mitscherlich finds that permanganate and perchlorate of potassa are isomorphous, an observation confirmed by Mr. Miller.

Protochloride of Manganese.—This compound is best prepared by evaporating a solution of the chloride to dryness by a gentle heat, and heating the residue to redness in a glass tube, while a current of hydrochloric acid gas is transmitted through it. The heat of a spirit-lamp is sufficient for the purpose. It fuses readily at a red heat, and forms a pink-coloured lamellated mass on cooling. It is deliquescent, and of course very soluble in water.

Perchloride of Manganese.—Dumas discovered this compound, which is readily formed by putting a solution of permanganic into strong sulphuric acid, and then adding fused sea-salt. The hydrochloric and permanganic acids mutually decompose each other; water and perchloride of manganese are generated, and the latter escapes in the form of vapour. The best mode of preparation is to form the green mineral chameleon, and acidulate with sulphuric acid: the solution, when evaporated, leaves a residue of sulphate and permanganate of potassa. This mixture, treated by strong sulphuric acid, yields a solution of permanganic acid, into which are added small fragments of sea-salt, as long as coloured vapour continues to be evolved. (Edin. Journ. of Science, viii. 179.)

The perchloride, when first formed, appears as a vapour of a copper or greenish colour; but on traversing a glass tube cooled to 5° or —4°, it is condensed into a greenish-brown coloured liquid. When generated in a capacious tube, its vapour gradually displaces the air, and soon fills the tube. If it is then poured into a large flask, the sides of which are moist, the colour of the vapour changes instantly on coming into contact with the moisture, a dense smoke of a pretty rose-tint appears, and hydrochloric and permanganic acids are generated. It is hence analogous in composition to permanganic acid, its elements being in such a ratio that

1 eq. perchloride and 7 eq. water yield 1 eq. permang. acid and 7 eq. hydrochloric acid.
$2Mn + 7Cl \qquad 7(H + O) \qquad 2Mn + 7O \qquad 7(H + Cl)$.

Perfluoride of Manganese.—This gaseous compound, discovered by Dumas and Wöhler (Edin. Journ. of Science, ix.), is best formed by mixing common mineral chameleon with half its weight of fluor spar, and decomposing the mixture in a platinum vessel by fuming sulphuric acid. The fluoride is then disengaged in the form of a greenish-yellow gas or vapour, of a more intensely yellow tint than chlorine. When mixed with atmospheric air, it instantly acquires a beautiful purple-red colour; and it is freely absorbed by water, yielding a solution of the same red tint. It acts instantly on glass, with formation of fluosilicic acid gas, a brown matter being at the same time deposited, which becomes of a deep purple-red tint on the addition of water.

It may be inferred from the experiments of Wöhler that this yellow gas is a fluoride of manganese; that when mixed with water both compounds are decomposed, and hydrofluoric and permanganic acids generated, which are dissolved; that a similar formation of the two acids ensues from the admixture of the yellow gas with atmospheric air, owing to the moisture contained in the latter; and that by contact with glass, fluosilicic acid gas is produced, and anhydrous permanganic acid deposited. In consequence of its acting so powerfully on glass, its other properties have not been ascertained; but from those above mentioned, its composition is obviously similar to that of the gaseous chloride of manganese.

Protosulphuret of Manganese may be procured by igniting the sulphate with one-sixth of its weight of charcoal in powder. (Berthier.) It is also formed by the action of hydrosulphuric acid gas on the protosulphate at a red heat. (Arfwedson in Ann. of Phil. vol. vii. N. S.) It occurs native in Cornwall, and at Naygag in Transylvania. It dissolves completely in dilute sulphuric or hydrochloric acid, with disengagement of very pure hydrosulphuric acid gas.

SECTION XII.

IRON.

Iron has been known from the remotest antiquity. It has a peculiar gray colour, and strong metallic lustre, which is susceptible of being heightened by polishing. In ductility and malleability it is inferior to several metals, but exceeds them all in tenacity. (Page 282.) At common temperatures it is very hard and unyielding, and its hardness may be increased by being heated and then suddenly cooled; but it is at the same time rendered brittle. When heated to redness it is remarkably soft and pliable, so that it may be beaten into any form, or be intimately incorporated or *welded* with another piece of red-hot iron by hammering. Its texture is fibrous. Its specific gravity may be estimated at 7.7; but it varies slightly according to the degree with which it has been rolled, hammered, or drawn, and it is increased by fusion. In its pure state it is exceedingly infusible, requiring for fusion the highest temperature of a wind furnace. It is attracted by the magnet, and may itself be rendered permanently magnetic by several processes;—a property of great interest and importance, and which is possessed by no other metal excepting cobalt and nickel.

The occurrence of native iron, except that of meteoric origin, which always contains nickel and cobalt, is exceedingly rare; and few of the specimens said to be such have been well attested. In combination, however, especially with oxygen and sulphur, it is abundant; being contained in animals and plants, and being diffused so universally in the earth, that there are few mineral substances in which its presence may not be detected. Minerals which contain iron in such form, and in such quantity, as to be employed in the preparation of the metal, are called *ores of iron;* and of these the principal are the following. The red oxides of iron, included under the name of red hæmatite; the brown hæmatite of mineralogists, consisting of hydrated peroxide of iron; the black oxide, or magnetic iron ore; and carbonate of protoxide of iron, either pure, or in the form of clay iron ore, when it is mixed with siliceous, aluminous, and other foreign substances. The three former occur most abundantly in primary districts, and supply the finest kinds of iron, as those of Sweden and India; while clay-iron stone, from which most of the English iron is extracted, occurs in secondary deposites, and chiefly in the coal formation.

The extraction of iron from its ores is effected by exposing the ore, previously roasted and reduced to a coarse powder, to the action of charcoal or coke, and lime at a high temperature. The action of carbonaceous matter in depriving the ore of its oxygen is obvious; and the lime plays a part equally important. It acts as a flux by combining with all the impurities of the ore, and forming a fusible compound called a *slag*. The whole mass being thus in a fused state, the particles of reduced metal descend by reason of their greater density, and collect at the bottom; while the slag forms a stratum above, protecting the melted metal from the action of the air. The latter, as it collects, runs out at an aperture in the side of the furnace; and the fused iron is let off by a hole in the bottom, which was previously filled with sand. The process is never successful unless the flux, together with the impurities of the ore, are in such proportion as to constitute a fusible compound. The mode of accomplishing this object is learned only by experience; and as different ores commonly differ in the nature or quantity of their impurities, the workman is obliged to vary his flux according to the composition of the ore with which he operates. Thus if the ore is deficient in siliceous matter, sand must be added; and if it contain a large quantity of lime, proportionally less of that earth will be required. Much is often accomplished by the admixture of different ores with each other. The slag consists of a compound of earthy salts, similar to some siliceous minerals, in which silicic acid is combined with lime, alumina, magnesia, protoxide of manganese, and sometimes oxide of iron. The most usual combination, according to Mitscherlich, is bisilicate of lime and magnesia, sometimes with a little protoxide of iron; a compound which he has obtained in crystals, having the precise form and composition of pyroxen. Artificial minerals may in fact by such processes be procured, similar in form and composition to those which occur in the earth. We are indebted to Mitscherlich for some valuable facts on this subject. (An. de Ch. et de Ph. xxiv. 355.)

The iron obtained by this process is the cast iron of commerce, and contains a considerable quantity of carbon, unreduced ore, and earthy substances. It is converted into soft or malleable iron by exposure to a strong heat while a current of air plays upon its surface. By this means any undecomposed ore is reduced, earthy impurities rise to the surface as slag, and carbonaceous matter is burned. The exposed iron is also more or less oxidized at its surface, and the resulting oxide, being stirred with the fused metal below, facilitates the oxidation of the carbon. As the purity of the iron increases, its fusibility diminishes, until at length, though the temperature continue the same, the iron becomes solid. It is then subjected, while still hot, to the operation of rolling or hammering, by which its particles are approximated, and its tenacity greatly increased. It is then the malleable iron of commerce. It is not, however, absolutely pure; for Berzelius has detected in it about one-half per cent. of carbon, and it likewise contains traces of silicium. The carbonaceous matter may be removed by mixing iron filings with a quarter of its weight of black oxide of iron, and fusing the mixture, confined in a covered Hessian crucible, by means of a blast furnace. A little powdered green glass should be laid on the mixture, in order that the iron may be completely protected from the air by a covering of melted glass, and any unreduced oxide dissolved. But the best and readiest mode of procuring iron in a state of perfect purity, is by transmitting hydrogen gas over the pure oxide heated to redness in a tube of porcelain. The oxygen of the oxide unites with hydrogen, and the metal is left in the form of a porous spongy mass. Magnus has observed that the reduction takes place at a heat considerably below that of redness; and that when the iron, thus reduced, is exposed to the air, it takes fire spontaneously, and the oxide is instantly reproduced. This singular property, which Magnus has also remarked in nickel and cobalt prepared in a similar manner, appears to depend on the extremely divided and expanded state of the metallic mass; for when the reduction is effected at a red heat, which enables the metal to acquire its natural degree of compactness, the phenomenon is not observed. If the oxide be mixed with a little alumina, and then reduced at a red heat, the presence of the earth prevents that contraction which would otherwise ensue: the metal is in the same mechanical condition as when it is deoxidized at a low temperature, and its spontaneous combustibility is preserved.

But iron, in its ordinary state, has a strong affinity for oxygen. In a perfectly dry atmosphere it undergoes no change; but when moisture is likewise present, its oxidation, or *rusting*, is rapid. In the first part of the change carbonate of protoxide of iron is generated; but the protoxide gradually passes into hydrated peroxide, and the carbonic acid at the same time is evolved. Rust of iron always contains ammonia, a circumstance which indicates that the oxidation is probably accompanied by decomposition of water; and M. Chevalier has observed that ammonia is also present in the native oxides of iron. Heated to redness in the open air, iron absorbs oxygen rapidly, and is converted into black scales, called the *black oxide* of iron; and in an atmosphere of oxygen gas it burns with vivid scintillations. It decomposes the vapour of water, by uniting with its oxygen, at all temperatures, from a dull red to a white heat; a singular fact, when it is considered, that, at the very same temperatures, the oxides of iron are reduced to the metallic state by hydrogen gas. (Gay-Lussac in An. de Ch. et de Physique, i. 36.) These opposite effects, various instances of which are known to chemists, are accounted for by a mode of reasoning similar to that explained on a former occasion. (Page 131.)

The equivalent of iron has not yet been determined with accuracy. From the analysis of its oxides by Berzelius, Stromeyer, and Gay-Lussac, it may be estimated at 27.16, 27.8, and 28.3. In the uncertainty as to which of these numbers is the most accurate, I shall continue to use 28, the number generally adopted in this country. The composition of the compounds of iron described in this section is as follows:—

	Iron.				Equiv.	Formulæ.
Protoxide	28	1 eq.+Oxy.	8	1 eq.	= 36	$Fe+O$ or $\dot{Fe}$.
Peroxide	56	2 eq.+do.	24	3 eq.	= 80	$2Fe+3O$ or $\underline{\dddot{Fe}}$.
Black oxide	Protoxide . . .		36	1 eq.	=116	$\dot{Fe}+\underline{\dddot{Fe}}$.
	Peroxide . . .		80	1 eq.		
Protochloride	28	1 eq.+Chlor.	35.42	1 eq.	= 63.42	$Fe+Cl$ or $FeCl$.
Perchloride	56	2 eq.+do.	106.26	3 eq.	=162.26	$2Fe+3Cl$ or Fe^2Cl^3.
Protiodide	28	1 eq.+Iodine	126.3	1 eq.	=154.3	$Fe+I$ or FeI.
Periodide	56	2 eq.+do.	378.9	3 eq.	=434.9	$2Fe+3I$ or Fe^2I^3.
Protobromide	28	1 eq.+Brom.	78.4	1 eq.	=106.4	$Fe+Br$ or $FeBr$.
Perbromide	56	2 eq.+do.	235.2	3 eq.	=291.2	$2Fe+3Br$ or Fe^2Br^3.
Protofluoride	28	1 eq.+Fluor.	18.68	1 eq.	= 46.68	$Fe+F$ or FeF.
Perfluoride	56	2 eq.+do.	56.04	3 eq.	=112.04	$2Fe+3F$ or Fe^2F^3.
Tetrasulphuret	112	4 eq.+Sulph.	16.1	1 eq.	=128.1	$4Fe+S$ or Fe^4S.
Disulphuret	56	2 eq.+do.	16.1	1 eq.	= 72.1	$2Fe+S$ or Fe^2S.
Protosulphuret	28	1 eq.+do.	16.1	1 eq.	= 44.1	$Fe+S$ or FeS.
Sesquisulphuret	56	2 eq.+do.	48.3	3 eq.	=104.3	$2Fe+3S$ or Fe^2S^3.
Bisulphuret	28	1 eq.+do.	32.2	2 eq.	= 60.2	$Fe+2S$ or FeS^2.
Magnetic pyrites	Bisulph. of iron		60.2	1 eq.	=280.7	$5FeS+FeS^2$.
	Protosulph. of iron		220.5	5 eq.		
Diphosphuret	56	2 eq.+Phosp.	15.7	1 eq.	= 71.7	$2Fe+P$ or Fe^2P.
Perphosphuret	84	3 eq.+do.	62.8	4 eq.	=146.8	$3Fe+4P$ or Fe^3P^4.
Carburets.	Constitution not determined.					

	Iron.				Equiv.	Formulæ.
Protocyanuret	28	1 eq.+	Cyan.	26.39	1 eq.=54.39	$Fe+Cy$ or $FeCy$.
Protosulphocyanuret	28	1 eq.	Cyan. 26.39 Sulph. 32.2	58.59	1 eq.=86.59	$Fe+CyS^2$.
Sesquisulphocyanuret	56	2 eq.	Bisulph. of cyanogen	175.77	3 eq.=231.77	$2Fe+3CyS^2$.

OXIDES OF IRON.

Protoxide.—This oxide is the base of the native carbonate of iron, and of the green vitriol of commerce. Its existence was inferred some years ago by Gay-Lussac; (An. de Ch. vol. lxxx.) but it is doubtful if it has ever been obtained in an insulated form. Its salts, particularly when in solution, absorb oxygen from the atmosphere with such rapidity that they may even be employed in eudiometry. This protoxide is always formed with evolution of hydrogen gas when metallic iron is put into dilute sulphuric acid; and its composition may be determined by collecting and measuring the gas which is disengaged.

Protoxide of iron is precipitated from its salts as a white hydrate by pure alkalies, as a white carbonate by alkaline carbonates, and as a white ferrocyanuret by ferrocyanuret of potassium. The two former precipitates become first green and then red, and the latter, green and blue by exposure to the air. The solution of gall-nuts produces no change of colour. Hydrosulphuric acid does not act if the protoxide is united with any of the stronger acids; but alkaline hydrosulphates cause a black precipitate, protosulphuret of iron.

Peroxide.—The red or peroxide is a natural product, known to mineralogists under the name of *red hæmatite.* It sometimes occurs massive, at other times fibrous, and occasionally in the form of beautiful rhomboidal crystals. It may be made chemically by dissolving iron in nitro-hydrochloric acid, and adding an alkali. The hydrate of the red oxide of a brownish-red colour subsides, which is identical in composition with the mineral called *brown hæmatite*, and consists of 80 parts or one equivalent of the peroxide, and 18 parts or two equivalents of water.

Peroxide of iron is not attracted by the magnet. Fused with vitreous substances, it communicates to them a red or yellow colour. It combines with most of the acids, forming salts, the greater number of which are red. Its presence may be detected by very decisive tests. The pure alkalies, fixed or volatile, precipitate it as the hydrate. Alkaline carbonates have a similar effect, peroxide of iron not forming a permanent salt with carbonic acid. With ferrocyanuret of potassium it forms Prussian blue. Sulphocyanuret of potassium causes a deep blood-red, and infusion of gall-nuts, a black colour. Hydrosulphuric acid converts the peroxide into protoxide of iron, with deposition of sulphur. These reagents, and especially ferrocyanuret and sulphocyanuret of potassium, afford an unerring test of the presence of minute quantities of peroxide of iron. On this account it is customary, in testing for iron, to convert it into the peroxide, an object which is easily accomplished by boiling the solution with a small quantity of nitric acid.

Black Oxide.—This substance, the *oxidum ferroso-ferricum* of Berzelius, long supposed to be protoxide of iron, contains more oxygen than the protoxide, and less than the red oxide. It cannot be regarded as a definite compound of iron and oxygen; but it is composed of the two real oxides united in a proportion which is by no means constant. It occurs native, frequently crystallized in the form of a regular octohedron; and it is not only attracted by the magnet, but is itself sometimes magnetic. It is always formed when iron is heated to redness in the open air; and is likewise generated by the contact of watery vapour with iron at elevated temperatures.

The composition of the product, however, varies with the duration of the process and the temperature which is employed. Thus, according to Bucholz, Berzelius, and Thomson, 100 parts of iron, when oxidized by steam, unite with nearly 30 of oxygen; whereas in a similar experiment performed by Gay-Lussac, 37.8 parts of oxygen were absorbed. The oxide of Gay-Lussac has the composition stated in the table; and Berzelius thinks that of magnetic iron ore to be similar. M. Mosander states, that on heating a bar of iron in the open air, the outer layer of the scales contains a greater quantity of peroxide than the inner layer. The former consists of one equivalent of peroxide to four of the protoxide, and in the latter are contained one equivalent of peroxide to six equivalents of protoxide. The inner layer seems uniform in composition; but the outer is variable, its more exposed parts being richer in oxygen.

The nature of the black oxide is farther elucidated by the action of acids. On digesting the black oxide in sulphuric acid, an olive-coloured solution is formed, containing two salts, sulphate of the peroxide and protoxide, which may be separated from each other by means of alcohol. (Proust and Gay-Lussac.) The solution of these mixed salts gives green precipitates with alkalies, and a very deep blue ink with infusion of gall-nuts. The black oxide of iron is the cause of the dull green colour of bottle glass.

Protochloride of Iron.—This compound is formed by transmitting dry hydrochloric acid gas over iron at a red heat, when hydrogen gas is evolved and the surface of the iron is covered with a white crystalline protochloride which at a stronger heat is sublimed. Also, on acting with hydrochloric acid on iron, which is dissolved with evolution of hydrogen gas, evaporating to dryness, and heating to redness in a tube without exposure to the air, a gray crystalline protochloride is left; but it contains some protoxide formed by an interchange of elements between the last portions of water and the chloride, hydrochloric acid being also generated.

Protochloride of iron dissolves freely in water, yielding a pale green solution, from which rhomboidal prisms of the same colour are obtained by evaporation. The crystals contain several equivalents of water of crystallization, deliquesce by exposure to the air, owing to the formation of perchloride, and are soluble in alcohol as well as water. The aqueous solution absorbs oxygen from the air, and becomes yellow from the formation of perchloride of iron: one portion of iron takes oxygen from the air, and yields its chlorine to another portion of iron, whereby perchloride and peroxide of iron are generated, and the latter falls as an ochreous sediment combined with some of the perchloride. A solution of the protochloride of iron dissolves binoxide of nitrogen with the same phenomena as the protosulphate (page 178), a circumstance favourable to the view entertained by many that protochloride of iron is converted by water into hydrochlorate of the protoxide.

Perchloride of Iron.—It is formed by the combustion of iron wire in dry chlorine gas, and by transmitting that gas over iron moderately heated; when it is obtained in small iridescent plates of a red colour, which are volatile at a heat a little above 212°, deliquesce readily, and dissolve in water, alcohol, and ether. On agitating ether with a strong aqueous solution of the perchloride, the ether abstracts a part of it, and acquires a gold-yellow colour. The readiest mode of obtaining a solution of the perchloride is to dissolve peroxide of iron in hydrochloric acid. On concentrating to the consistence of syrup and cooling, it separates as red crystals, which by distillation yield at first water and hydrochloric acid, and then anhydrous perchloride of iron, leaving a compound of peroxide and perchloride of iron in crystalline laminæ. The formation of peroxide appears due to an interchange of elements between it and water. The same kind of interchange ensues between the vapours of water and the perchloride at a high temperature; and this is probably the source, as Mitscherlich suggests, of the crystals of peroxide of iron found in volcanic products.

Protiodide of Iron.—It exists as a pale green solution when iodine is digested with water and iron wire, the latter being in excess; and on evaporating the solution, without exposure to the air, to dryness, and heating moderately, the protiodide is fused, and on cooling becomes an opaque crystalline mass of an iron-gray colour and metallic lustre. It is deliquescent and very soluble in water and alcohol. Its aqueous solution attracts oxygen rapidly from the air, undergoing the same kind of change as the protochloride: to preserve a solution of protiodide as such, a long piece of iron wire should be kept permanently in the liquid. This compound has been very successfully employed in medical practice by my colleague Dr. A. T. Thomson.

The *periodide*, of a yellow or orange colour according to the strength of the solution, is obtained by freely exposing a solution of the protiodide to the air, or digesting iron wire with excess of iodine, gently evaporating, and subliming the periodide. It is a volatile red compound, deliquescent, and soluble in water and alcohol.

The *bromides* of iron are formed under similar conditions to the chlorides and iodides, and are very analogous to them in their properties.

Protofluoride of Iron is best prepared by dissolving iron in a solution of hydrofluoric acid, out of which it crystallizes as the acid becomes saturated, in small white square tables, which are sparingly soluble in water, and become pale yellow by the action of the air. By heat they part with their water of crystallization, and afterwards bear a red heat without decomposition. (Berzelius.)

The *perfluoride* is formed by dissolving peroxide of iron in hydrofluoric acid, and yields a colourless solution even when saturated. By evaporation it is left as a crystalline mass of a pale flesh-colour, and of a mild astringent taste. It is sparingly soluble in water.

Sulphurets of Iron.—These elements have for each other a remarkably strong affinity, and unite under various circumstances and in several proportions. The two lowest degrees of sulphuration, the *tetrasulphuret* and *disulphuret*, were prepared by Arfwedson by transmitting a current of hydrogen gas, at a red heat, over the anhydrous disulphate of peroxide of iron to procure the tetrasulphuret, and over anhydrous sulphate of protoxide of iron for the disulphuret. In both cases sulphurous acid and water are evolved, and the resulting sulphurets are left as grayish-black powders, susceptible of a metallic lustre by friction. They both dissolve in dilute sulphuric acid with evolution of hydrogen and hydrosulphuric acid gases.

Protosulphuret of Iron is prepared by heating thin laminæ of iron to redness with sulphur in a covered Hessian crucible, and continuing the heat until any excess of sulphur is expelled. The iron is found with a crust of protosulphuret, which is brittle, of a yellowish-gray colour and metallic lustre, and is attracted by the magnet. When pure it is completely dissolved by dilute sulphuric acid, yielding pure hydrosulphuric acid. The protosulphuret of iron exists in nature as an ingredient in variegated copper pyrites; and it falls on mixing hydrosulphate of ammonia with sulphate of protoxide of iron as a black precipitate, which oxidizes rapidly by absorbing oxygen from the air, as soon as the excess of hydrosulphate of ammonia is removed by washing.

The *sesquisulphuret* is formed in the moist way by adding perchloride of iron drop by drop to hydrosulphate of ammonia or sulphuret of potassium in excess, and falls as a black precipitate, which is oxidized readily by the air. In the dry way it is slowly produced by the action of hydrosulphuric acid gas on peroxide of iron at a heat not exceeding 212°, water being also formed; and by the action of the same gas on the hydrated peroxide at common temperatures. This sulphuret, when anhydrous, has a yellowish-gray colour, is not attracted by the magnet, and dissolves in dilute sulphuric or hydrochloric acid, yielding hydrosulphuric acid and a residue of bisulphuret of iron. (Berzelius.)

Bisulphuret of Iron, *iron pyrites* of mineralogists, exists abundantly in the earth. It occurs in cubes or some allied form, has a yellow colour, metallic lustre, a density of 4.981, and is so hard that it strikes fire with steel. Some varieties have a white colour; but these usually contain arsenic. Others occur in rounded nodules, have a radiated structure divergent from a common centre, are often found in beds of clay, and are much disposed by the influence of air and moisture to yield sulphate of oxide of iron: these are suspected by Berzelius to be compounds of protosulphuret and bisulphuret of iron.

Bisulphuret of iron is not attacked by any of the acids except the nitric, and its best solvent is the nitro-hydrochloric acid. Heated in close vessels it gives off nearly half its sulphur, and is converted into magnetic iron pyrites. By heat and air together it yields peroxide of iron.

Magnetic Iron Pyrites.—This is a natural product, termed magnetic pyrites from being attracted by the magnet, and was formerly regarded as protosulphuret of iron; but Stromeyer has shown that its elements are in such a ratio, that it may be regarded as a compound of bisulphuret and protosulphuret. It is formed by heating the bisulphuret to redness in close vessels, by fusing iron filings with half their weight of sulphur, or by rubbing sulphur upon a rod of iron heated to whiteness. It is soluble in dilute sulphuric acid, yielding hydrosulphuric acid gas and a residue of sulphur. It is much more oxidable by air and moisture than the pure bisulphuret.

Diphosphuret of Iron.—It is prepared by exposing the phosphate of protoxide of iron to a strong heat in a covered crucible lined with charcoal, the excess of phosphorus being dissipated in vapour. It is a fused granular mass, of the colour and lustre of iron, but very brittle, and is not attacked by hydrochloric acid. It is sometimes contained in metallic iron, to the properties of which it is very injurious by rendering it brittle at common temperatures.

The *perphosphuret* has been obtained by Rose by the action of phosphuretted hydrogen gas on sulphuret of iron at a moderate temperature, and resembles the former in its properties.

Carburets of Iron.—Carbon and iron unite in very various proportions; but there are three compounds very distinct from each other—namely, graphite, cast or pig iron, and steel.

Graphite, also known under the name of *plumbago* and *black-lead*, occurs not unfrequently as a mineral production, and is found in great purity at Borrowdale in Cumberland. It may be made artificially by exposing iron with excess of charcoal to a violent and long-continued heat; and it is commonly generated in small quantity during the preparation of cast iron. Pure specimens contain about four or five per cent. of iron, but sometimes its quantity amounts to 10 per cent. Most chemists believe the iron to be chemically united with the charcoal; but according to the researches of Dr. Karsten of Berlin, native graphite is only a mechanical mixture of charcoal and iron, while artificial graphite is a real carburet.

Graphite is exceedingly unchangeable in the air, and like charcoal is attacked with difficulty by chemical reagents. It may be heated to any extent in close vessels without change; but if exposed at the same time to the air, its carbon is entirely consumed, and oxide of iron remains. It has an iron-gray colour, metallic lustre, and granular texture; and it is soft and unctuous to the touch. Its chief use is in the manufacture of pencils and crucibles; and in burnishing iron to protect it from rust.

Cast iron is the product of the process for extracting iron from its ores, and is commonly regarded as a real compound of iron and charcoal. It always contains impurities, such as charcoal, undecomposed ore, and earthy matters, which are often visible by mere inspection; and sometimes traces of chromium, manganese, sulphur, phosphorus, and arsenic are present. It fuses readily at 2786° F. (Daniell), which is a full red heat, and in cooling it acquires a crystalline granular texture. The quality of different specimens is by no means uniform; and two kinds, white and gray cast iron, are in particular distinguished from each other. The former is exceedingly hard and brittle, sometimes breaking like glass from sudden change of temperature; while the latter is softer and much more tenacious. This difference appears owing to the mode of combination, rather than to a difference in the proportion of carbon; for the white variety may be converted into the gray by exposure to a strong heat and cooling slowly, and the gray may be changed into the white by being heated and rapidly cooled. According to Karsten, the carbon of the latter is combined with the whole mass of iron, and amounts as a maximum to 5.25 per cent; but in some specimens its proportion is considerably less. The former, on the contrary, contains from 3.15 to 4.65 per cent. of carbon, of which about three-fourths are in the state of graphite, and are left as such after the iron is dissolved by acids; while the remaining fourth is in combination with the whole mass of metal, constituting a carburet which is very similar to steel. Gray cast iron may hence be regarded as a kind of steel, in which graphite is mechanically mixed.

Steel is commonly prepared in this country by the process of cementation, which consists in filling a large furnace with alternate strata of bars of the purest malleable iron and powdered charcoal, closing every aperture so as perfectly to exclude atmospheric air, and keeping the whole during several days at a red heat. By this treatment the iron gradually combines with from 1.3 to 1.75 per cent. of carbon, its texture is greatly changed, and its surface is blistered. It is subsequently hammered at a red heat into small bars, and may be welded either with other bars of steel or with malleable iron. Mr. Mackintosh of Glasgow has introduced an elegant process of forming steel by exposing heated iron to a current of coal gas; when carburetted hydrogen is decomposed, its carbon enters into combination with iron, and hydrogen gas is evolved.

In ductility and malleability it is far inferior to iron; but exceeds it greatly in hardness, sonorousness, and elasticity. Its texture is also more compact, and it is susceptible of a higher polish. It sustains a full red heat without fusing, and is, therefore, less fusible than cast iron; but it is much more so than malleable iron. By fusion it forms cast steel, which is more uniform in composition and texture, and possesses a closer grain than ordinary steel.

Protocyanuret of Iron.—This compound is obtained as a yellow hydrate by mixing in solution cyanuret of potassium with sulphate of protoxide of iron; but by the action of the air, it passes into Prussian blue. Berzelius obtains it as a yellowish-gray powder by heating in a tube the double cyanuret of iron and hydrocyanate of ammonia until the latter is expelled.

Protosulphocyanuret of Iron.—Hydrosulphocyanic acid dissolves iron with evolution of hydrogen gas, yielding a pale green solution, which may be obtained in a dry state by evaporation in vacuo. Atmospheric oxygen reddens it rapidly, and an ochreous sediment falls.

Sesquisulphocyanuret of Iron.—This compound, of a blood-red colour, is formed by mixing in solution any salt of the peroxide of iron with sulphocyanuret of potassium, its intense colour affording a very delicate test of iron (page 277). By dissolving hydrated peroxide of iron in hydrosulphocyanic acid, and evaporating, the sesquisulphocyanuret is obtained as a red mass, deliquescent, and soluble in water and alcohol.

SECTION XIII.

ZINC.—CADMIUM.

ZINC.

This metal was first mentioned under the term *zinetum* in the sixteenth century by Paracelsus; but it was probably known at a much earlier period.

In commerce it is often called *spelter*, and is obtained either from *calamine*, native carbonate of zinc, or from the native sulphuret, *zinc blende* of mineralogists. It is procured from the former by heat and carbonaceous matters; and from the latter by a similar process after the ore has been previously oxidized by *roasting*, that is, by exposure to the air at a low red heat. Its preparation affords an instance of what is called *distillation by descent*. The furnace or crucible for reducing the ore is closed above, and in its bottom is fixed an iron tube, the upper aperture of which is in the interior of the crucible, and its lower terminates just above a vessel of water. The vapour of zinc, together with all the gaseous products, passes through this tube, and the zinc is condensed. The first portions are commonly very impure, containing cadmium and arsenic, the period of their disengagement being indicated by what the workmen call the *brown blaze;* but when the *blue blaze* begins, that is, when the metallic vapour burns with a bluish-white flame, the zinc is collected. As thus obtained, it is never quite pure: it frequently contains traces of charcoal, sulphur, cadmium, arsenic, lead, and copper; and iron is always present. It may be freed from these impurities by distillation,—by exposing it to a white heat in an earthen retort, to which a receiver full of water is adapted; but the first portions, as liable to contain arsenic and cadmium, should be rejected.

Zinc has a strong metallic lustre, and a bluish-white colour. Its texture is lamellated, and its density about 7. It is a hard metal, being acted on by the file with difficulty. At low or high degrees of heat it is brittle; but at temperatures between 210° and 300° F. it is both malleable and ductile, a property which enables zinc to be rolled or hammered into sheets of considerable thinness. Its malleability is considerably diminished by the impurities which the zinc of commerce contains. It fuses at 773° F. (Daniell), and when slowly cooled crystallizes in four or six-sided prisms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes little change by the action of air and moisture. When fused in open vessels it absorbs oxygen, and forms the white oxide, called flowers of zinc. Heated to full redness in a covered crucible, it bursts into flame as soon as the cover is removed, and burns with a brilliant white light. The combustion ensues with such violence, that the oxide as it is formed is mechanically carried up into the air. The heat at which it begins to burn is estimated by Daniell at 941° F. Zinc is readily oxidized by dilute sulphuric or hydrochloric acid, and the hydrogen which is evolved contains a small quantity of metallic zinc in combination.

Gay-Lussac and Berzelius found that the protoxide of zinc consists of 100 parts of metallic zinc and 24.8 of oxygen, being a ratio of 32.3 to 8. Its other combinations justify the adoption of 32.3 as the equivalent of zinc. The composition of its compounds described in this section is as follows:—

	Zinc.				Equiv.	Formulæ.
Protoxide	32.3	1 eq. + Oxygen	8	1 eq. =	40.3	$Zn+O$ or $\dot{Zn}$.
Peroxide	Composition uncertain.					
Chloride	32.3	1 eq. + Chlorine	35.42	1 eq. =	67.72	$Zn+Cl$ or $ZnCl$.
Iodide	32.3	1 eq. + Iodine	126.3	1 eq. =	158.6	$Zn+I$ or ZnI.
Bromide	32.3	1 eq. + Bromine	78.4	1 eq. =	110.7	$Zn+Br$ or $ZnBr$.
Fluoride	32.3	1 eq. + Fluorine	18.68	1 eq. =	50.98	$Zn+F$ or ZnF.
Sulphuret	32.3	1 eq. + Sulphur	16.1	1 eq. =	48.4	$Zn+S$ or ZnS.
Cyanuret	32.3	1 eq. + Cyanogen	26.39	1 eq. =	58.69	$Zn+Cy$ or $ZnCy$.

Protoxide of Zinc.—This is the only oxide of zinc which acts as a salifiable base, and the only one of known composition. It is generated during the solution of zinc in dilute sulphuric acid, and may be obtained in a dry state by collecting the flakes which rise during the combustion of zinc, or by heating the carbonate to redness. At common temperatures it is white; but when heated to low redness, it assumes a yellow colour, which gradually disappears on cooling. It is quite fixed in the fire. It is insoluble in water, and, therefore, does not affect the blue colour of plants; but it is a strong salifiable base, forming regular salts with acids, most of which are colourless. It combines also with some of the alkalies.

The presence of zinc is easily recognized by the following characters.— The oxide is precipitated from its solutions as a white hydrate by pure potassa or ammonia, and as carbonate by carbonate of ammonia, but is completely redissolved by an excess of the precipitant. The fixed alkaline carbonates precipitate it permanently as white carbonate of oxide of zinc. Hydrosulphate of ammonia causes a white precipitate, a hydrated sulphuret of zinc. Hydrosulphuric acid acts in a similar manner, if the solution is quite neutral; but it has no effect if an excess of any strong acid is present.

When metallic zinc is exposed for some time to air and moisture, or is kept under water, it acquires a superficial coating of a gray matter, which Berzelius describes as a sub-oxide. It is probably a mixture of metallic zinc and the white oxide, into which it is resolved by the action of acids. The peroxide is prepared, according to Thenard, by acting on hydrated white oxide of zinc with peroxide of hydrogen diluted with water. It resolves itself so readily into oxygen and the oxide already described, that it cannot be preserved even under the surface of water; and its composition is quite unknown.

Chloride of Zinc.—This compound is formed, with evolution of heat and light, when zinc filings are introduced into chlorine gas; and it is readily prepared by dissolving zinc in hydrochloric acid, evaporating to dryness, and heating the residue in a tube through which dry hydrochloric acid gas is transmitted. It is colourless, fusible at a heat a little above 212°, has a soft consistence at common temperatures, hence called *butter of zinc*, sublimes at a red heat, and deliquesces in the air.

Iodide of Zinc is prepared by digesting iodine in water with zinc filings in excess. A colourless solution results, which by evaporation yields a deliquescent iodide. By heat in close vessels it may be sublimed, and then crystallizes in brilliant needles; but if heated in the open air, oxide of zinc is formed, and iodine expelled. If zinc is digested in water with an excess of iodine, a brown solution results, which probably contains a biniodide.

Bromide of Zinc may be formed by a process similar to that for the iodide, but its properties have not been studied.

Fluoride of Zinc is obtained by acting directly on oxide of zinc with hydrofluoric acid, and is a white compound of sparing solubility.

Sulphuret of Zinc.—This compound is well known to mineralogists under the name of *zinc blende*, and occurs in dodecahedral crystals or some allied form. Its structure is lamellated, lustre adamantine, and colour variable, being sometimes yellow, red, brown, or black. It may be formed artificially by igniting, in a closed crucible, a mixture of oxide of zinc and sulphur, or sulphate of oxide of zinc and charcoal, or by drying the hydrated sulphuret of zinc.

CADMIUM.

Cadmium so called (from καδμεία, a term applied both to calamine and to the volatile matters which rise from the furnace in preparing brass) because it is associated with zinc, was discovered in the year 1817 by Stromeyer in an oxide of zinc which had been prepared for medical use; and he has since found it in several of the ores of that metal, especially in a radiated blende from Bohemia, which contains about five per cent. of cadmium. The late Dr. Clarke detected its existence in some of the zinc ores of Derbyshire, and in the common zinc of commerce. Mr. Herapath has found it in considerable quantity in the zinc works near Bristol. During the reduction of calamine by coal, the cadmium, which is very volatile, flies off in vapour mixed with soot and some oxide of zinc, and collects in the roof of the vault, just above the tube leading from the crucible. Some portions of this substance yielded from 12 to 20 per cent. of cadmium. (An. of Phil. xiv. and xvii.)

The process by which Stromeyer separates cadmium from zinc or other metals is the following. The ore of cadmium is dissolved in dilute sulphuric or hydrochloric acid, and after adding a portion of free acid, a current of hydrosulphuric acid gas is transmitted through the liquid, by which means the cadmium is precipitated as sulphuret, while the zinc continues in solution. The sulphuret of cadmium is then decomposed by nitric acid, and the solution evaporated to dryness. The dry nitrate is dissolved in water, and an excess of carbonate of ammonia added. The white carbonate of oxide of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with charcoal, and exposing the mixture to a red heat, metallic cadmium is sublimed.

A very elegant process for separating zinc from cadmium was proposed by Wollaston. The solution of the mixed metals is put into a platinum capsule, and a piece of metallic zinc is placed in it. If cadmium is present, it is reduced, and adheres so tenaciously to the capsule, that it may be washed with water without danger of being lost. It may then be dissolved either by nitric or dilute hydrochloric acid.

Cadmium, in colour and lustre, has a strong resemblance to tin, but is somewhat harder and more tenacious. It is very ductile and malleable. Its specific gravity is 8.604 before being hammered, and 8.694 afterwards. It melts at about the same temperature as tin, and is nearly as volatile as mercury, condensing like it into globules which have a metallic lustre. Its vapour has no odour. When heated in the open air, it absorbs oxygen, and is converted into an oxide. Cadmium is readily oxidized and dissolved by nitric acid, which is its proper solvent. Sulphuric and hydrochloric acids act upon it less easily, and the oxygen is then derived from water.

The equivalent of cadmium, deduced from Stromeyer's analysis of its oxide, is 55.8. The composition of its compounds described in this section is as follows:—

	Cadmium.					Equiv.	Formulæ.
Oxide of Cadm.	55.8	1 eq. +	Oxygen	8	1 eq. =	63.8	$Cd + O$ or $\dot{Cd}$.
Chloride	55.8	1 eq. +	Chlorine	35.42	1 eq. =	91.22	$Cd + Cl$ or $CdCl$.
Iodide	55.8	1 eq. +	Iodine	126.3	1 eq. =	182.1	$Cd + I$ or CdI.
Sulphuret	55.8	1 eq. +	Sulphur	16.1	1 eq. =	71.9	$Cd + S$ or CdS.

Oxide of Cadmium.—This, the only known oxide of cadmium, is prepared by igniting its carbonate, has an orange colour, is fixed in the fire, and is insoluble in water. It has no action on test paper, but is a strong alkaline base, forming neutral salts with acids. It is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of that alkali. It is precipitated permanently by pure potassa or soda as a hydrate, and by all the alkaline carbonates as carbonate of oxide of cadmium.

Chloride of Cadmium.—By dissolving oxide of cadmium in hydrochloric acid and concentrating duly, the chloride with water of crystallization crystallizes in transparent four-sided rectangular prisms, which lose their water by heat and even in a dry air, fuse at a heat short of redness, and acquire a lamellated texture in cooling. At a high temperature it is sublimed.

Iodide of Cadmium may be formed in the same manner as iodide of zinc, is soluble in water and alcohol, and crystallizes by evaporation in large, colourless, transparent, hexagonal tables, which do not change in the air, and have a pearly lustre. By heat they lose water and then fuse.

Sulphuret of Cadmium occurs in mixture or combination in some kinds of zinc blende, and is easily prepared by the action of hydrosulphuric acid on a salt of cadmium. It has a yellowish-orange colour, and is distinguished from the sulphurets of arsenic by being insoluble in pure potassa, and by sustaining a white heat without subliming. (Stromeyer.)

SECTION XIV.

TIN.

Tin was known to the ancients, who obtained it principally, if not solely, from Cornwall. The tin of commerce is distinguished into two varieties, called *block* and *grain tin*, both of which are procured from the native oxide by means of heat and charcoal. In Cornwall, which has been celebrated for its tin mines during many centuries, the ore is both extracted from veins, and found in the form of rounded grains among beds of rolled materials, which have been deposited by the action of water. These grains, commonly called *stream tin*, contain a very pure oxide, and yield the purest kind of grain tin. An inferior sort is prepared by heating bars of tin, extracted from the common ore, to very near their point of fusion, when the more fusible parts, which are the purest, flow out; and the less fusible portions constitute block tin. The usual impurities are iron, copper and arsenic.

Tin has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is but very slowly impaired by exposure to the atmosphere, nor is it oxidized even by the combined agency of air and moisture. Its malleability is very considerable; for the thickness of common tin-foil does not exceed 1-1000th of an inch. In ductility and tenacity it is inferior to several metals. It is soft and inelastic, and when bent backwards and forwards, emits a peculiar crackling noise. Its specific gravity is about 7.2. At 442° F. it fuses, and if exposed at the same time to the air, its surface tarnishes, and a gray powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into peroxide of tin.

The equivalent of tin deduced by Berzelius from his analysis of its oxides is 57.9. The composition of the compounds of tin described in this section is as follows:—

	Tin.				Equiv.	Formulæ.
Protoxide .	57.9	1 eq.+	Oxygen	8	1 eq.= 65.9	$Sn+O$ or $\dot{Sn}$.
Sesquioxide	115.8	2 eq.+	do.	24	3 eq.=139.8	$2Sn+3O$ or $\overset{\cdots}{\underline{Sn}}$.
Binoxide .	57.9	1 eq.+	do.	16	2 eq.= 73.9	$Sn+2O$ or $\ddot{Sn}$.
Protochloride	57.9	1 eq.+	Chlorine	35.42	1 eq.= 93.32	$Sn+Cl$ or $SnCl$.
Bichloride .	57.9	1 eq.+	do.	70.84	2 eq.=128.74	$Sn+2Cl$ or $SnCl^2$.
Protiodide .	57.9	1 eq.+	Iodine	126.3	1 eq.=184.2	$Sn+I$ or SnI.
Biniodide .	57.9	1 eq.+	do.	252.6	2 eq.=310.5	$Sn+2I$ or SnI^2.
Protosulphuret	57.9	1 eq.+	Sulphur	16.1	1 eq.= 74.	$Sn+S$ or SnS.
Sesquisulph.	115.8	2 eq.+	do.	48.3	3 eq.=164.1	$2Sn+3S$ or Sn^2S^3.
Bisulphuret	57.9	1 eq.+	do.	32.2	2 eq.= 90.1	$Sn+2S$ or SnS^2.
Terphosphuret	57.9	1 eq.+	Phosph.	47.1	3 eq.=105.	$Sn+3P$ or SnP^3.

Protoxide of Tin.—When chloride of tin in solution is mixed with an alkaline carbonate, hydrated oxide of tin falls, which may be obtained as such in a dry form by washing with warm water, and drying at a heat not above 196°, with the least possible exposure to the air. This hydrate is white, burns like tinder when suddenly heated, and is decomposed by being boiled in water. The best mode of obtaining the anhydrous oxide is by heating the hydrate to redness in a tube from which air is excluded by a current of carbonic acid gas. The same oxide is formed when tin is kept for some time fused in an open vessel.

Protoxide of tin has a sp. gravity of 6.666. At common temperatures it is permanent in the air, but if touched by a red hot body, it takes fire and is converted into the peroxide. It is dissolved by the sulphuric and hydrochloric acids, as also by dilute nitric acid; and the pure fixed alkalies likewise dissolve it. From the alkaline solution, metallic tin is gradually deposited, and peroxide of tin remains in solution. Its salts are remarkably prone to absorb oxygen, both from the air and from compounds which yield oxygen readily. Thus it converts peroxide of iron into protoxide, and throws down mercury, silver, and platinum in the metallic state from their salts. With a solution of gold it causes a purple precipitate, the *purple of Cassius*, which appears to be a compound of peroxide of tin and protoxide of gold. By this character protoxide of tin is recognized with certainty. It is thrown down by hydrosulphuric acid as black protosulphuret of tin.

Sesquioxide of Tin.—Fuchs has lately succeeded in preparing this oxide by mixing recently precipitated and moist hydrated peroxide of iron with a solution of protochloride of tin as free as possible from hydrochloric acid; when by an interchange of elements

1 eq. perox. iron &	2 eq. chloride of tin	yield	1 eq. sesquiox. tin &	2 eq. chlo. iron.
$2Fe+3O$	$2(Sn+Cl)$		$2Sn+3O$	$2(Fe+Cl)$.

The sesquioxide falls as a slimy gray matter, and in general rather yellow from adhering oxide of iron. Berzelius obtained it purer by using a solution made by saturating hydrochloric acid as far as possible with hydrated peroxide of iron. The sesquioxide of tin, while moist, is soluble in hydrochloric acid, and the solution strikes the purple of Cassius with gold; and it is readily soluble in a solution of ammonia, which distinguishes it from the protoxide of tin, just as its action on gold does from the binoxide. (Pog. Annalen, xxviii. 443.)

Binoxide of Tin is most conveniently prepared by the action of nitric acid on metallic tin. Nitric acid, in its most concentrated state, does not act easily upon tin; but when a small quantity of water is added, violent effervescence takes place owing to the evolution of nitrous acid and binoxide of nitrogen, and a white powder, the hydrated binoxide, is produced. On edulcorating this substance, and heating it to redness, watery vapour is expelled, and the pure binoxide, of a straw-yellow colour, remains. In this process ammonia is generated, a circumstance which proves water as well as nitric acid to be decomposed. Binoxide of tin may likewise be obtained by precipitation from a solution of perchloride of tin by potassa, ammonia, or the alkaline carbonates; but in this case it falls as a very bulky hydrate, different from the other hydrate both in appearance and several of its chemical properties. Thus the latter dissolves readily in sulphuric, nitric, and hydrochloric acid, even when diluted; while the former is completely insoluble in the same acids, even when concentrated. It unites, indeed, with hydrochloric acid, and the compound is soluble in pure water.

Binoxide of tin has very little disposition in any state to unite with acids, and, when dissolved by them, is very apt to separate itself spontaneously as a gelatinous hydrate. It acts the part of a feeble acid: it reddens litmus when its hydrate moistened is laid upon it, and it unites with the pure alkalies, forming soluble compounds which are called *stannates*.

Binoxide of tin is recognized by its insolubility in acids in its anhydrous state; by separating from its solution by means of hydrochloric acid as a bulky hydrate by any of the alkalies or alkaline carbonates, which is easily and completely dissolved by pure potassa or soda in excess; and by yielding with hydrosulphuric acid the yellow bisulphuret of tin, which is also soluble in pure potassa.

Binoxide of tin, when melted with glass, forms a white enamel.

Protochloride of Tin.—This compound is obtained by transmitting hydrochloric acid gas over metallic tin heated in a glass tube, when hydrogen gas is evolved; or by distilling a mixture either of granulated tin with an equal weight of bichloride of mercury, or of an amalgam of tin with calomel, urging the heat till the mercury is expelled. In this state it is a gray solid, of a resinous lustre, which fuses below redness, and at a high temperature sublimes. It is obtained by crystallization from a concentrated solution of the chloride in crystals, which are sometimes in small white needles, and at others in large transparent prisms, and consist of 93.32 parts or one eq. of protochloride of tin and 27 parts or three eq. of water. On heating these crystals, they not only lose water, but reaction ensues between the elements of water and the chloride, hydrochloric acid gas is evolved, and protoxide of tin remains combined with the chloride. The same kind of compound is formed when a large quantity of the water is poured upon the crystals: the solution contains protochloride of tin and hydrochloric acid, and a white powder subsides which consists of one eq. of the protochloride, one eq. of protoxide, and two eq. of water. (Berzelius.)

A solution of protochloride of tin is obtained by heating granulated tin in strong hydrochloric acid as long as hydrogen gas continues to be evolved. This solution is much employed as a deoxidizing agent, being more powerful than the sulphate or nitrate of the protoxide; owing apparently to the tendency of the protochloride of tin to resolve itself into bichloride and metallic tin, the latter taking oxygen or chlorine from any metallic solutions which yield them readily.

Bichloride of Tin.—When protochloride of tin is heated in chlorine gas, or on distilling a mixture of 8 parts of granulated tin with 24 of bichloride of mercury, a very volatile, colourless liquid passes over, which is bichloride of tin. In an open vessel it emits dense white fumes, caused by the moisture of the air, and hence it was formerly called the *fuming liquor* of Libavius, who discovered it. At 248° it boils, and the sp. gravity of its vapour was found by Dumas to be 9.1997. With one-third of its weight of water it forms a solid hydrate, and in a larger quantity of water dissolves.

The solution of bichloride of tin, commonly called *permuriate of tin*, is much used in dyeing, and is prepared by dissolving tin in nitro-hydrochloric acid. The process requires care; for if the action be very rapid, as is sure to happen if strong acid be employed and much tin added at once, the peroxide will be spontaneously deposited as a bulky hydrate, and be subsequently redissolved with great difficulty. But the operation will rarely fail if the acid is made with two measures of hydrochloric acid, one of nitric acid, and one of water, and if the tin is gradually dissolved, one portion disappearing before another is added. The most certain mode of preparation, however, is to prepare a solution of the protochloride, and convert it into the bichloride either by chlorine, or by gentle heat and nitric acid.

Iodides of Tin.—The *protiodide* is formed by heating granulated tin with about 2½ times its weight of iodine, and is a brownish-red, translucid substance, very fusible, volatile at a high temperature, and soluble in water.

The *biniodide* is prepared by dissolving in hydriodic acid the hydrate of the peroxide, precipitated by alkalies from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin.

Protosulphuret of Tin.—This compound is prepared by pouring melted tin upon its own weight of sulphur, and stirring rapidly with a stick during the action; as some tin usually escapes the sulphur from the latter being rapidly expelled, the product should be pulverized, mixed with its weight of sulphur, and projected in successive portions into a hot Hessian crucible, and then heated to redness. It is a brittle compound, of a bluish-gray, nearly black, colour and metallic lustre, which fuses at a red heat, and acquires a lamellated texture in cooling. It is dissolved by hydrochloric acid with evolution of hydrosulphuric acid. The same sulphuret is obtained in the moist way by adding hydrosulphuric acid to a solution of protochloride of tin. The *sesquisulphuret* is formed by mixing the protosulphuret in fine powder with a third of its weight of sulphur, and heating the mixture to low redness until sulphur ceases to escape. Its colour is of a deep grayish-yellow; it is reconverted by a strong heat into the protosulphuret, and dissolves in hydrochloric acid gas, yielding hydrosulphuric acid gas and a residue of bisulphuret of tin.

Bisulphuret of Tin, formerly called *mosaic gold*, is prepared by heating in a glass or earthen retort a mixture of 2 parts of peroxide of tin, 2 of sulphur, and 1 part of sal ammoniac, and maintaining a low red heat until sul-

is acid ceases to be evolved. These materials are sometimes employed
t sal ammoniac, but Berzelius says that the latter is essential for ob-
g the bisulphuret. The product when successfully prepared, is in crys-
scales, and sometimes even in regular six-sided tables, of a golden-
colour and metallic lustre. It is soluble in pure potassa and in its
ate by boiling; but its only solvent among the acids is the nitro-
hloric. The bisulphuret is obtained as a bulky hydrate of a dirty
colour by the action of hydrosulphuric acid or hydrosulphate of am-
on bichloride of tin in solution.

hosphuret of Tin.—Rose formed this compound by acting on a solu-
protochloride of tin by phosphuretted hydrogen. It is readily oxidized
action of the air.

SECTION XV.

COBALT.—NICKEL.

COBALT.

s metal is met with in the earth chiefly in combination with arsenic,
uting an ore from which all the cobalt of commerce is derived. It is a
nt ingredient of meteoric iron, though in very small quantity. (Stro-
.) Its name is derived from the term *Kobold, an evil spirit*, applied
y the German miners at a time when they were ignorant of its value,
nsidered it unfavourable to the presence of valuable metals.

en native arseniuret of cobalt is broken into small pieces, and exposed
verberatory furnace to the united action of heat and air, its elements
idized, most of the arsenious acid is expelled in the form of vapour,
impure oxide of cobalt, called *zaffre*, remains. On heating this sub-
with a mixture of sand and potash, a beautiful blue-coloured glass is
d, which, when reduced to powder, is known by the name of *smalt*.

allic cobalt may be obtained by dissolving zaffre in hydrochloric acid,
nsmitting through the solution a current of hydrosulphuric acid gas
e arsenious acid is completely separated in the form of orpiment.
tered liquid is then boiled with a little nitric acid, in order to convert
toxide into peroxide of iron, and an excess of carbonate of potassa is
The precipitate, consisting of peroxide of iron and carbonate of pro-
f cobalt, after being well washed with water, is digested in a solution
c acid, which dissolves the oxide of iron and leaves the oxide of co-
he form of an insoluble oxalate. (Laugier.) On heating this oxalate
rt from which atmospheric air is excluded, a large quantity of car-
id is evolved, and a black powder, metallic cobalt, is left. (Thomson
ls of Philosophy, N. S. i.) The pure metal is easily procured also by
a current of dry hydrogen gas over oxide of cobalt heated to redness
of porcelain. In this state it is porous, and if formed at a low
ure it inflames spontaneously, as stated in the section on iron (page

tion of cobalt may also be made by acting on the native arseniuret
huric mixed with a fourth part of nitric acid, separating as much
acid as possible by evaporation, and conducting the remainder of
ss as above described. The arseniuret from Tunaberg should be
for this purpose, as it is in general free from nickel, which always
ies the cobalt ores of Germany.

is a brittle metal, of a reddish-gray colour, and weak metallic lustre.
y, according to my observation, is 7.834. It fuses at a heat rather
iron, and when slowly cooled it crystallizes. It is attracted by

the magnet, and is susceptible of being rendered permanently magnetic. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or hydrochloric acid, but is readily oxidized by means of nitric acid. Like iron and the other metals of this order, it decomposes water at a red heat with disengagement of hydrogen gas. (Despretz.)

According to the analyses of Rothoff on the oxides of cobalt, its equivalent is inferred to be 29.5 (Ann. of Phil. iii. 356.) The composition of its compounds described in this section is as follows:—

	Cobalt.			Equiv.	Formulæ.
Protoxide	29.5	1 eq. + Oxygen	8	1 eq.= 37.5	Co + O or $\dot{Co}$.
$\frac{4}{3}$ Oxide	88.5	3 eq. + do.	32	4 eq.=120.5	3Co + 4O or Co^3O^4.
Peroxide	59	2 eq. + do.	24	3 eq.= 83	2Co + 3O or $\underline{\dddot{Co}}$.
Chloride	29.5	1 eq. + Chlor.	35.42	1 eq.= 64.92	Co + Cl or $\overline{CoCl}$
Protosulphuret	29.5	1 eq. + Sulphur	16.1	1 eq.= 45.6	Co + S or CoS.
Sesquisulphuret	59	2 eq. + do.	48.3	3 eq.=107.3	2Co + 3S or Co^2S^3.
Bisulphuret	29.5	1 eq. + do.	32.2	2 eq.=61.7	Co + 2S or CoS^2.
Subphosphuret	88.5	3 eq. + Phosp.	31.4	2 eq.=119.9	3Co + 2P or Co^3P^2.

Protoxie of Cobalt.—This oxide is of an ash-gray colour, and is the basis of the salts of cobalt, most of which are of a pink hue. When heated to redness in open vessels it absorbs oxygen, and is converted into the peroxide. It may be prepared by decomposing carbonate of the protoxide by heat in a vessel from which atmospheric air is excluded. It is easily recognized by giving a blue tint to borax when melted with it; and is employed in the arts, in the form of smalt, for communicating a similar colour to glass, earthenware, and porcelain.

Protoxide of cobalt is precipitated from its salts by pure potassa as a blue hydrate, which absorbs oxygen from the air, and gradually acquires a dirty green tint. Pure ammonia likewise causes a blue precipitate, which is redissolved by the alkali if in excess. It is thrown down as a pale pink carbonate by carbonate of potassa, soda, or ammonia; but an excess of the last redissolves it with facility. Hydrosulphuric acid produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphates always precipitate it as a black protosulphuret of cobalt.

$\frac{4}{3}$*Oxide of Cobalt.*—It is said that when protoxide of cobalt, or the nitrate, carbonate, or oxalate of that oxide, is gently ignited in an open fire, peroxide of cobalt results; but M. Hess has lately shown that the oxide then obtained is analogous in composition to the red oxide of manganese. The peroxide of cobalt is converted into it, with loss of oxygen, by a full red heat, whether exposed to the air or not; so that of the oxides of cobalt it is the most stable. The same compound is obtained as a dirty green hydrate by the action of the air on the hydrated protoxide. It is probably a compound of peroxide and protoxide of cobalt, since 3Co+4O obviously contain the elements $\dot{Co}+\underline{\dddot{Co}}$. This intermediate oxide is of a dark brown colour, and does not unite with acids or alkalies. (Pog. Annalen, xxvi. 542.)

Peroxide.—This oxide is obtained as a black hydrate containing two eq. of water, $\underline{\dddot{Co}}+2\dot{H}$, when chloride of cobalt in solution is decomposed by chloride of lime, or chlorine is transmitted into water in which hydrated protoxide of cobalt is suspended. In this case

3 eq. protoxide & 1 eq. chlorine yield 1 eq. peroxide & 1 eq. Chloride
$3(Co+O)$ $Cl.$ $2Co+3O$ $Co+Cl.$

This hydrate has a black colour, and yields the black anhydrous peroxide by exposure to a heat of 600° or 700°; but it is difficult to drive off all the water, without also losing oxygen. It combines with none of the acids, and when digested with hydrochloric acid it emits chlorine gas, and chloride of cobalt is generated.

When a salt of cobalt is treated with pure ammonia in close vessels, part of the cobalt is dissolved, and part subsides in form of a blue powder. On admitting atmospheric air, this substance passes to a higher state of oxidation, and is gradually dissolved. If nitrate of cobalt is used, a double salt may be obtained in crystals, which L. Gmelin, to whom we are indebted for these remarks, believes to consist of nitrate and *cobaltate* of ammonia. The existence of this acid, however, has not yet been satisfactorily established.

Chloride of Cobalt.—It is obtained in solution on dissolving metallic cobalt, its protoxide, or either of the other oxides in hydrochloric acid, with evolution of hydrogen gas with the first and of chlorine with the latter. It yields a pink-coloured solution, and by evaporation small crystals of the same colour containing water of crystallization. When deprived of water its colour is blue, a character on which is founded its use as a sympathetic ink: when letters are written with a dilute solution of the chloride, the colour is so pale that it is invisible in the cold; but on heating gently, the letters appear of a blue colour, and disappear as soon as the chloride has recovered its moisture from the atmosphere. When iron or nickel is present, the dry chloride of cobalt is green instead of blue.

Sulphurets.—Cobalt appears to unite with sulphur in three proportions; the first being a protosulphuret, the second a sesquisulphuret, and the third a bisulphuret. The protosulphuret has a gray colour, a metallic lustre, and a crystalline texture. It may be formed in the dry way either by throwing fragments of sulphur on red-hot cobalt, or by igniting protoxide of cobalt with sulphur; and it is thrown down as a black precipitate from the salts of cobalt by alkaline hydrosulphates, or even by hydrosulphuric acid gas if the salt is quite neutral, or the oxide united with any of the feebler acids.

Arfwedson has observed that when hydrogen gas is transmitted over sulphate of oxide of cobalt heated to redness, water and sulphurous acid are evolved, and a compound remains, called an *oxysulphuret*, consisting of oxide of cobalt united with sulphuret of cobalt. When this substance is exposed to hydrosulphuric acid gas at a red heat, the oxide is decomposed, and the sesquisulphuret is formed.

The bisulphuret is prepared, according to Setterberg, by heating 2 parts of carbonate of oxide of cobalt intimately mixed with 3 parts of sulphur. The process is conducted in a glass retort, and the heat continued as long as sulphur is expelled; but the temperature should not be suffered to reach that of redness.

Subphosphuret of Cobalt.—Rose obtained this phosphuret by the action of hydrogen gas on subphosphate of oxide of cobalt heated in a tube, water being also generated. In this case

1 eq. phosphate and 8 eq. hydrogen yield 1 eq. phosphuret and 8 eq. water.
$3(Co+O)+(2P+5O)$ $8H$ $3Co+2P$ $8(H+O).$

This phosphuret is pulverulent and of a gray colour, and is also obtained by the action of phosphuretted hydrogen gas on chloride of cobalt.

NICKEL.

Nickel is a constituent of meteoric iron; but its principal ore is the copper coloured mineral of Westphalia, termed *kupfer-nickel*, *copper nickel*; *nickel* being an epithet of detraction, applied by the older German miners, because the mineral looked like an ore of copper, and yet they could extract none from it. The preparations of nickel may either be prepared from copper nickel, which is an arseniuret of nickel containing small quantities of sulphur, copper, cobalt, and iron, or from the artificial arseniuret called *speiss*, a metallurgic production obtained in forming smalt from the roasted ores of cobalt. Various processes have been devised for procuring a pure salt of nickel, but the following appears to me as simple and perhaps as successful as any. After reducing speiss to fine powder, it is digested in sulphuric acid, to which a fourth part of nitric acid is added; and when the solution is saturated with nickel, it is set aside for several hours in order that arsenious acid may separate, and is then filtered. The clear liquid is subsequently mixed with a solution of sulphate of potassa, and set aside to crystallize spontaneously; when a double salt, sulphate of oxide of nickel and potassa is deposited. Dr. Thomson, who proposed this process, states that the crystals thus obtained are quite free from arsenic and iron, and contain no impurities except copper and cobalt. The former is precipitated as sulphuret by a current of hydrosulphuric acid gas, a little free sulphuric acid being previously added; and at the same time any traces of arsenic, if present, would likewise subside as orpiment. The filtered liquor is then heated to expel free hydrosulphuric acid, and the oxides of nickel and cobalt precipitated by carbonate of potassa. The separation of these oxides may then be effected by the method suggested by Berthier; namely, by precipitating them together by pure potassa, and, after washing the mixed hydrates, suspending them in water through which chlorine gas is transmitted to saturation. All the cobalt and generally some nickel is converted into peroxide and thus rendered insoluble; while the greater part of the nickel is dissolved in the form of chloride, and may be removed from the insoluble peroxides by filtration.

Metallic nickel, which may be prepared either by heating the oxalate in close vessels, or by the combined action of heat and charcoal or hydrogen on oxide of nickel, is of a white colour, intermediate between that of tin and silver. It has a strong metallic lustre, and is both ductile and malleable. It is attracted by the magnet, and like iron and cobalt may be rendered magnetic. Its specific gravity after fusion is about 8.279, and is increased to near 9.0 by hammering.

Nickel is very infusible, but less so than pure iron. It suffers no change at common temperatures by exposure to air and moisture; but it absorbs oxygen at a red heat, though not rapidly, and is partially oxidized. It decomposes water at the same temperature. Hydrochloric and sulphuric acids act upon it with difficulty; but by nitric acid it is readily oxidized, and forms a nitrate of the protoxide of nickel.

From the analyses of the oxides of nickel by Rothoff and Tupputi, the equivalent of nickel may be estimated at 29.5. The composition of its compounds described in this section is as follows:—

	Nickel.					Equiv.	Formulæ.
Protoxide	29.5	1 eq. +	Oxygen	8	1 eq. =	37.5	Ni + O or $\dot{Ni}$.
Peroxide	59	2 eq. +	do.	24	3 eq. =	83	2Ni + 3O or $\dddot{Ni}$.
Chloride	29.5	1 eq. +	Chlorine	35.42	1 eq. =	64.92	Ni + Cl or $Ni\overline{Cl}$.
Protosulphuret	29.5	1 eq. +	Sulphur	16.1	1 eq. =	45.6	Ni + S or NiS.
Disulphuret	59	2 eq. +	do	16.1	1 eq. =	75.1	2Ni + S or Ni^2S.
Subphosphuret	88.5	3 eq. +	Phos.	31.4	2 eq. =	119.9	3Ni + 2P or Ni^3P^2.
Cyanuret.	29.5	1 eq. +	Cyanog.	26.39	1 eq. =	55.89	Ni + Cy or NiCy.

Protoxide of Nickel.—This oxide may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel, and is then of an ash-gray colour; but after exposure to a white heat, its colour is a dull olive-green. It is not reducible by heat unaided by combustibles. It is not attracted by the magnet. It is a strong alkaline base, and nearly all its salts have a green tint. It is precipitated as a hydrate of a pale-green colour by the pure alkalies, but is redissolved by ammonia in excess; as a pale green carbonate by alkaline carbonates, but is dissolved by an excess of carbonate of ammonia; and as a black sulphuret by alkaline hydrosulphates. Hydrosulphuric acid occasions no precipitate, unless the solution is quite neutral, or the oxide combined with a weak acid.

Peroxide.—this oxide has a black colour, and is formed by transmitting chlorine gas through water in which the hydrate of the protoxide is suspended. The peroxide does not unite with acids, is decomposed by a red heat, and with hot hydrochloric acid forms the chloride with disengagement of chlorine gas.

Thenard succeeded in preparing a peroxide by the action of peroxide of hydrogen on hydrated protoxide of nickel; but it is uncertain whether the composition of this peroxide is identical with that above described, or different. Two suboxides have likewise been enumerated; but their existence is exceedingly problematical.

Chloride of Nickel.—This compound is formed by acting with hydrochloric acid on metallic nickel, its protoxide, or peroxide; hydrogen gas being evolved with the former, and chlorine with the latter. It forms an emerald-green solution, and by evaporation yields crystals of the same tint, which lose water or deliquesce, according as the air is dry or moist. In its anhydrous state it is yellow; but a small admixture with cobalt causes a green tint. At a low red heat it sublimes, and condenses in brilliant scales of a gold-yellow colour.

Protosulphuret of Nickel is formed by processes similar to those described for preparing protosulphuret of cobalt. The precipitated sulphuret is dark brown or nearly black, and is dissolved by hydrochloric acid with evolution of hydrosulphuric acid; while that procured in the dry way is of a grayish-yellow colour, and requires for solution nitric or nitro-hydrochloric acid. It occurs as a natural production in very delicate acicular crystals, the *haarkies* of the Germans.

Arfwedson obtained the *disulphuret* by transmitting hydrogen gas over sulphate of oxide of nickel at a red heat. It is of a lighter yellow and more fusible than the former.

Subphosphuret of Nickel.—Rose obtained it by the action of hydrogen gas on subphosphate of oxide of nickel, the same change ensuing as with cobalt; and it is generated by the action of phosphuretted hydrogen gas on chloride of nickel. It has a black colour, is insoluble in hydrochloric acid, but dissolves in nitric acid. Heated by the blowpipe it burns with flame.

Cyanuret of Nickel.—It is obtained by mixing in solution a salt of nickel with cyanuret of potassium, and falls as a pale apple-green precipitate, which acquires a yellow tint in drying.

CLASS II.

ORDER II.

METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.

SECTION XVI.

ARSENIC.

Metallic arsenic sometimes occurs native, but more frequently it is found in combination with other metals, and especially with cobalt and iron. On roasting these arsenical ores in a reverberatory furnace, the arsenic, from its volatility, is expelled, combines with oxygen as it rises, and condenses into thick cakes on the roof of the chimney. The sublimed mass, after being purified by a second sublimation, is the virulent poison known by the name of *arsenic*, or *white oxide of arsenic*. From this substance the metal itself is procured by heating it with charcoal. The most convenient process is to mix the white oxide with about twice its weight of black flux, and expose the mixture to a red heat in a Hessian crucible, over which is luted an empty crucible for receiving the metal. The reduction is easily effected, and metallic arsenic collects in the upper crucible, which should be kept cool for the purpose of condensing the vapour.

Arsenic is an exceedingly brittle metal, of a strong metallic lustre, and white colour, running into steel-gray. Its structure is crystalline, and when slowly sublimed it is said to crystallize in rhombohedrons. Its sp. gravity is 5.8843. When heated to 356°, it sublimes without previously liquefying; for its point of fusion is far above that of its sublimation, and has not hitherto been determined. Its vapour has a strong odour of garlic, a property which affords a distinguishing character for metallic arsenic, as it is not possessed by any other metal, with the exception perhaps of zinc, which is said to emit a similar odour when thrown in powder on burning charcoal. In close vessels it may be sublimed without change, but if atmospheric air be admitted it is rapidly converted into the white oxide. According to Hahneman it is slowly oxidized and dissolved by being boiled in water. In general it speedily tarnishes by exposure to air and moisture, acquiring upon its surface a dark film, which is extremely superficial; but Berzelius remarks that he has kept some specimens in open vessels for years without loss of lustre, while others are oxidized through their whole substance, and fall into powder. The product of this spontaneous oxidation, which is known abroad under the name of *fly-powder*, is supposed by Berzelius to be an oxide; but it is more generally regarded as a mixture of white oxide and metallic arsenic.

The equivalent of arsenic, as inferred by Berzelius from the composition of arsenious and arsenic acids, is 37.7. The compounds of this metal described in this section are thus constituted:—

	Arsenic.		Equiv.	Formulæ.
Arsenious acid	75.4 2 eq. + Oxyg.	24	3 eq. = 99.4	2As + 3O or $\underline{\dddot{As}}$.
Arsenic acid	75.4 2 eq. + do.	40	5 eq. = 115.4	2As + 5O or $\underline{As}$.
Protochloride	37.7 1 eq. + Chlorine	35.42	1 eq. = 73.12	As + Cl or AsCl.

	Arsenic.			Equiv.	Formulæ.
Sesqui-chloride	75.4	2 eq. + Chlor.	106.26	3 eq. = 181.66	$2As + 3Cl$ or As^2Cl^3.
Periodide	75.4	2 eq. + Iodine	631.5	5 eq. = 706.9	$2As + 5I$ or As^2I^5.
Sesqui-bromide	75.4	2 eq. + Brom.	235.2	3 eq. = 310.6	$2As + 3Br$ or As^2Br^3.
Proto-hyduret	37.7	1 eq. + Hydr.	1	1 eq. = 38.7	$As + H$ or AsH.
Arsen. Hydr.	75.4	2 eq. + do	3	3 eq. = 78.4	$2As + 3H$ or As^2H^3.
Protosul-phuret	37.7	1 eq. + Sulph.	16.1	1 eq. = 53.8	$As + S$ or AsS.
Sesqui-sulphuret	75.4	2 eq. + do.	48.3	3 eq. = 123.7	$2As + 3S$ or As^2S^3.
Persul-phuret	75.4	2 eq. + do.	80.5	5 eq. = 155.9	$2As + 5S$ or As^2S^5.

Arsenious Acid.—This compound, frequently called *white arsenic* and *white oxide of arsenic*, is always generated when arsenic is heated in open vessels, and may be prepared by digesting the metal in dilute nitric acid. The white arsenic of commerce is derived from the native arseniurets of cobalt, being sublimed during the roasting of these ores for the preparation of zaffre, and it is purified by a second sublimation in iron vessels. It is commonly sold in a state of fine white powder; but when first sublimed, it is in the form of brittle masses, more or less transparent, colourless, of a vitreous lustre, and conchoidal fracture. This glass, which may also be obtained by fusion, gradually becomes opaque without undergoing any apparent change of constitution, either with respect to water or any other substance; but the change is certainly promoted by exposure to the atmosphere. Its sp. gravity is 3.7. At 380° it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. Its point of fusion is rather higher than that at which it sublimes; and, therefore, in order to be fused, it must either be heated under pressure, or its temperature be suddenly raised above 380°. Arsenious acid is *dimorphous*, that is, susceptible of assuming two crystalline forms belonging to different systems of crystallization. By slow sublimation in a glass tube, it is always obtained in distinct octohedral crystals of adamantine lustre and perfectly transparent. Its unusual form is that of six-sided scales derived from a rhombic prism, and was first lately found by Wöhler among the products in a manufacture of smalt: the conditions for enabling it to assume this form are unknown, and by subliming the crystals, they crystallized in octohedrons. (An. de Ch. et. de Ph. li. 201.)

The taste of arsenious acid is stated differently by different persons. It is prevalently thought to be acrid: but I am satisfied from personal observation that it may be deliberately tasted without exciting more than a very faint impression of sweetness, and perhaps of acidity. The acrid taste ascribed to it has probably been confounded with the local inflammation, by which its application, if of some continuance, is followed. (Christison on Poisons.) It reddens vegetable blue colours feebly, an effect which is best shown by placing the acid in powder on moistened litmus paper. It combines with salifiable bases, forming salts which are termed *arsenites*.

According to the experiments of Klaproth and Buchholz, 1000 parts of boiling water dissolve 77.75 of arsenious acid; and the solution, after having cooled to 60° F., contains only 30 parts. The same quantity of water at 60, when mixed with the acid in powder, dissolves only two parts and a half. Guibourt has lately observed that the transparent and opaque varieties of arsenic differ in solubility. He found that 1000 parts of temperate water dissolve, during 36 hours, 9.6 of the transparent, and 12.5 of the opaque variety: that the same quantity of boiling water dissolves 97 parts of the transparent variety, retaining 18 when cold, but takes up 115 of the opaque variety, and retains 29 on cooling. By the presence of organic substances, such as milk or tea, its solubility is materially impaired. (Christison on Poisons.)

When metallic arsenic is sharply heated with hydrate of potassa, pure hydrogen gas is evolved, and a mass is left consisting of arseniuret of potassium and arsenite of potassa, facts, which prove that a portion of arsenic is oxidized, and derives its oxygen partly from water and partly from potassa. If the heat is raised to redness, the arsenious acid is resolved into arsenic acid and metal, the former remaining as an arseniate, while the latter is expelled. Similar phenomena ensue with the hydrates of soda, baryta, and lime; except that with the two latter no arsenic acid is produced. (Soubeiran in An. de Ch. et de Ph. xliii. 410.)

The frequent exhibition of arsenious acid as a poison renders the detection of this compound an object of great importance to medical practitioners as well as to the chemist. In this as in all similar inquiries, the object to be held in view is the discovery of a few decisive characters, by means of which the poison may be distinguished from all other bodies; and when present but in small quantity, either in pure water, or in any fluids likely to be met with in the stomach, may with certainty be detected. The attention should be fixed on one or two tests of admitted value, and all others be set aside. With this feeling I shall indicate the mode of applying the three principal tests, namely, the ammoniaco-nitrate of silver, ammoniaco-sulphate of copper, and hydrosulphuric acid.

1. Arsenious acid is not precipitated by nitrate of oxide of silver, unless an alkali is present to neutralize the nitric acid. Ammonia is commonly employed for the purpose; but as arsenite of oxide of silver is very soluble in ammonia, an excess of the alkali would retain the arsenite in solution. To remedy this inconvenience, Mr. Hume, of Long Acre, proposed to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a rather strong solution of lunar caustic till the oxide of silver, at first thrown down, is *nearly* all dissolved. The liquid thus prepared contains the precise quantity of ammonia which is required; and when mixed with arsenious acid, two neutral salts result, the soluble nitrate of ammonia, and the insoluble yellow arsenite of oxide of silver. Ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. Phosphate of oxide of silver is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate is held almost entirely in solution by the free ammonia.

This test, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with sea salt, or animal and vegetable infusions, the arsenite of oxide of silver either does not subside at all, or is precipitated in so impure a state that its characteristic colour cannot be distinguished. Several methods have been proposed for obviating this source of fallacy; but Dr. Christison has shown, that this test, taken singly, cannot be relied on in practice.

2. Ammoniacal sulphate of copper, which is made by adding ammonia to a solution of sulphate of oxide of copper until the precipitate at first thrown down is nearly all redissolved, occasions with arsenious acid a green precipitate, which has been long used as a pigment under the name of *Scheele's green*. This test, though well adapted for detecting arsenious acid dissolved in pure water, is very fallacious when applied to mixed fluids. Dr. Christison has proved that ammoniacal sulphate of copper produces in some animal and vegetable infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas in other mixed fluids, such as tea and porter, to which arsenic has been previously added, it occasions none at all, if the arsenious acid is in small quantity. In some of these liquids, a free vegetable acid is doubtless the solvent; but arsenite of oxide of copper is also dissolved by tannin and perhaps by other vegetable as well as some animal principles.

3. When a current of hydrosulphuric acid gas is conducted through a solution of arsenious acid, the fluid immediately acquires a yellow colour, and in a short time becomes turbid, owing to the formation of orpiment, the sesquisulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as free hydrosulphuric acid is expelled by heating the solution, it subsides perfectly, and may easily be collected on a filter. One condition, however, must be observed in order to ensure success, namely, that the liquid does not contain a free alkali; for sulphuret of arsenic is dissolved with remarkable facility by pure potassa or ammonia. To avoid this fallacy, it is necessary to acidulate the solution with a little acetic or hydrochloric acid. Hydrosulphuric acid likewise acts on arsenic in all vegetable and animal fluids, if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because hydrosulphuric acid causes a yellow precipitate, that arsenic is present; since there are not less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might possibly be mistaken for orpiment. From these and all other substances whatever, the sulphuret of arsenic may be thus distinguished.—On drying the sulphuret, mixing it with black flux, and heating the mixture contained in a glass tube to redness by means of a spirit-lamp, decomposition ensues, and a metallic crust of an iron-gray colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube. This character alone is quite satisfactory; but it is easy to procure additional evidence, by reconverting the metal into arsenious acid, so as to obtain it in the form of resplendent octohedral crystals. This is done by holding that part of the tube to which the arsenic adheres about three-fourths of an inch above a very small spirit-lamp flame, so that the metal may be slowly sublimed. As it rises in vapour it combines with oxygen, and is deposited in crystals within the tube. The character of these crystals, with respect to volatility, lustre, transparency, and form, is so exceedingly well marked, that a practised eye may safely identify them, though their weight should not exceed the 100th part of a grain. This experiment does not succeed unless the tube be quite clean and dry.

The only circumstance which occasions a difficulty in the preceding process, is the presence of organic substances, which cause the precipitate to subside imperfectly, render filtration tedious, and froth up inconveniently during the reduction. Hence, if so abundant as materially to impede filtration and prevent the liquid from becoming clear, they should be removed before hydrosulphuric acid is employed. This is often sufficiently effected by acidulating with acetic acid, by which caseous and albuminous substances are coagulated; but a more complete separation is accomplished by evaporating the solution at a moderate heat to dryness, redissolving anew by boiling successive portions of distilled water on the residue, and then filtering the solution after it has cooled. Most of the organic matters are thus rendered insoluble. It is of course necessary towards the close of the desiccation to guard against too high a temperature, since otherwise the arsenic itself might be expelled. (Christison on Poisons, 2nd Edition, 252.)

It hence appears, that of these various tests for arsenic, the only one which gives uniform results, and is applicable to every case, is hydrosulphuric acid, followed by reduction. No substance, indeed, nor mixture of substances, is known to produce with all the three liquid tests the same precipitate as arsenic, and, therefore, their indications, *when taken conjointly*, can scarcely be considered otherwise than conclusive; but still to most persons the sight and characters of the metal itself afford a higher degree of evidence than the colour and appearance of precipitates, and it is certain that a quantity of arsenic which may be thrown down by hydrosulphuric acid, and obtained in the metallic state, might be insufficient to yield characteristic compounds when divided into three parts and examined by three different re-agents. The method for detecting arsenic should, therefore, be principally limited to the last:—all the rest may be dispensed with.

For this great improvement in the mode of testing for arsenious acid, we are indebted to Dr. Christison. By this process he discovered the presence of arsenious acid when mixed with complex fluids, such as tea, porter, and the like, in the proportion of one-fourth of a grain to an ounce; and more recently he has twice obtained so small a quantity as the 20th of a grain from the stomachs of people who had been poisoned with arsenic.

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of bitartrate of potassa with rather less than half its weight of nitre. The nitric and tartaric acids undergo decomposition and the solid product is charcoal derived from tartaric acid, and pure carbonate of potassa. As it contains a deliquescent salt, it should be kept in well stopped bottles. When this substance is employed in the reduction of arsenious acid or its salts, the charcoal is of course the decomposing agent; but the alkali is of use in retaining the arsenious acid until the temperature is sufficiently high for its decomposition. With sulphuret of arsenic, on the contrary, the alkali is the active principle, the potassium of which unites with sulphur and liberates the arsenic; but the charcoal operates usefully by facilitating the decomposition of the alkaline carbonate. The whole of the arsenic, however, is not sublimed; but part of it enters into union with potassium, and remains with the flux.

Arsenic Acid.—This compound is made by dissolving arsenious acid in concentrated nitric, mixed with a little hydrochloric acid, distilling in glass till it acquires the consistence of syrup, and then exposing it in a platinum crucible for some time to a heat somewhat short of low redness to expel the nitric acid. The acid thus prepared has a sour metallic taste, reddens vegetable blue colours, and with alkalies forms neutral salts, which are termed *arseniates.* It is much more soluble in water than arsenious acid, dissolving in five or six times its weight of cold, and in a still smaller quantity of hot water. It forms irregular grains when its solution is evaporated, but does not crystallize. If strongly heated it fuses into a glass which is deliquescent. When urged by a very strong red heat it is resolved into oxygen and arsenious acid. It is an active poison.

Arsenic acid is decomposed by hydrosulphuric acid gas, and yields a sulphuret of arsenic very like orpiment in colour, but containing a greater proportional quantity of sulphur. The soluble arseniates, when mixed with the nitrates of lead and silver, form insoluble arseniates, the former of which has a white, and the latter a brick-red colour. They dissolve readily in dilute nitric acid, and when heated with charcoal yield metallic arsenic.

Protochloride of Arsenic.—It is prepared, according to Dumas, by introducing into a tubulated retort a mixture of arsenious acid with ten times its weight of concentrated sulphuric acid; and after raising its temperature to near 212°, fragments of sea-salt are thrown in by the tubular. If the salt is added in successive small portions, scarcely any hydrochloric acid gas is evolved, and the pure chloride may be collected in cooled vessels. Towards the end of the process a little water frequently passes over with the chloride; but this hydrated portion does not mix with the anhydrous chloride, but swims on its surface. The hydrate may be decomposed, and a pure chloride obtained, by distilling the mixture from a sufficient quantity of concentrated sulphuric acid. Dumas considers this compound a protochloride of arsenic, so that it is probably different from that obtained by means of corrosive sublimate. (Quarterly Journal of Science, N. S. i. 235.)

Sesquichloride of Arsenic.—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire and sesquichloride of arsenic is generated; and the same compound may be formed by distilling a mixture of six parts of corrosive sublimate with one of arsenic. It is a colourless volatile liquid, which fumes strongly on exposure to the air, hence called *fuming liquor of arsenic,* and is resolved by water into hydrochloric and arsenious acids. (Dr. Davy.)

Periodide of Arsenic is formed by bringing its elements into contact, and promoting union by gentle heat. They form a deep-red compound, which is resolved into arsenic and hydriodic acids by the action of water. (Plisson in An. de Ch. et de Ph. xxxix. 266.)

Sesquibromide of Arsenic.—The elements of this compound unite at the moment of contact, with vivid evolution of heat and light. Serullas prepared it by adding dry arsenic to bromine as long as light was emitted, the former being added in successive small quantities, to prevent the temperature from rising too high. The bromide is then distilled, and collected in a cool receiver. (An. de Ch. et de Ph. xxxviii. 318.)

This compound is solid at or below 68°, liquifies between 68° and 77°, and boils at 428°. As a liquid it is transparent and slightly yellow, and yields long prisms by evaporation. By water it is resolved into arsenious and hydrobromic acids.

Protohyduret of Arsenic.—This compound, which is solid and of a brown colour, was discovered by Davy as well as Gay-Lussac and Thenard. The former prepared it by attaching a piece of arsenic to the negative wire during the decomposition of water by galvanism; and the French chemists, by the action of water on an alloy of potassium and arsenic.

Arseniuretted Hydrogen.—This gas, which was discovered by Scheele, has been studied by Proust, Trommsdorf, and others, but especially by Stromeyer. It is generally made by digesting an alloy of tin and arsenic in hydrochloric acid; but as thus prepared it is always mixed with free hydrogen. Soubeiran generated it by fusing arsenic with its own weight of granulated zinc, and decomposing the alloy with strong hydrochloric acid. The gas, thus developed, is quite free from hydrogen, being absorbed without residue by a saturated solution of sulphate of oxide of copper. Its sp. gravity, according to Dumas, is 2.695. It is colourless, and has a fetid odour like that of garlic. It extinguishes bodies in combustion, but is itself kindled by them, and burns with a blue flame. It instantly destroys small animals that are immersed in it, and is poisonous to man in a high degree, having proved fatal to a German philosopher, the late M. Gehlen. Water absorbs one-fifth of its volume, and acquires the odour of the gas. It wants altogether the properties of an acid.

Arseniuretted hydrogen is decomposed by various agents. It suffers gradual decomposition when mixed with atmospheric air, water being formed, and metallic arsenic, together with a little oxide, deposited. With nitric acid, water is generated, and a deposite of metal takes place, which is subsequently oxidized. Chlorine decomposes it instantly with disengagement of heat and light, hydrochloric acid being generated, and the metal set free. With iodine it yields hydriodic acid gas and iodide of arsenic, and sulphur and phosphorus produce analogous changes. By its action on salts of the easily reducible metals, such as silver and gold, the metal is revived, and its oxygen uniting with the elements of the gas constitutes arsenious acid and water. With salts of copper the products are water and arseniuret of copper; and with several other metallic salts its action is similar.

Soubeiran observed that arseniuretted hydrogen in a glass tube is completely decomposed by the heat of a spirit-lamp, and that its hydrogen occupies one and a half as much space as when in combination. He has also confirmed the observation of Dumas that when mixed with oxygen, and detonated by the electric spark, each volume of the gas, in forming water and arsenious acid, requires one and a half its volume of oxygen gas. The oxygen, therefore, is equally divided between the arsenic and hydrogen; and arseniuretted hydrogen consists of one equivalent of arsenic and one and a half of hydrogen. By volume, it is composed of quarter of a volume of the vapour of arsenic, and one and a half of hydrogen, condensed into one volume. (An. de Ch. et de Ph. xliii. 407.)

Sulphurets of Arsenic.—Sulphur unites with arsenic in at least three proportions, forming compounds, two of which occur in the mineral kingdom, and are well known by the names of *realgar* and *orpiment*. Realgar or the *protosulphuret* may be formed artificially by heating arsenious acid with about half its weight of sulphur, until the mixture is brought into a state of perfect fusion. The cooled mass is crystalline, transparent, and of a ruby red colour; and may be sublimed in close vessels without change.

Orpiment, or *sesquisulphuret* of arsenic, may be prepared by fusing together equal parts of arsenious acid and sulphur; but the best mode of obtaining it quite pure is by transmitting a current of hydrosulphuric acid gas through a solution of arsenious acid. Orpiment has a rich yellow colour, fuses readily when heated, and becomes crystalline on cooling, and in close vessels may be sublimed without change. It is dissolved with great facility by the pure alkalies, and yields colourless solutions.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow*. Braconnot has proposed it likewise for dyeing silk, woolen, or cotten stuffs of a yellow colour; the cloth being soaked in a solution of orpiment in ammonia, and then suspended in a warm apartment. The alkali evaporates, and leaves the orpiment permanently attached to the cloth. (An. de Ch. et de Ph. xii.)

Persulphuret of arsenic is prepared by transmitting hydrosulphuric acid gas through a moderately strong solution of arsenic acid; or by saturating a solution of arseniate of potassa or soda with the same gas, and acidulating with hydrochloric or acetic acid. The oxygen of the acid unites with the hydrogen of the gas, and presulphuret of arsenic subsides. In colour it is very similar to orpiment, is dissolved by pure alkalies, fuses by heat, and may be sublimed in close vessels without decomposition.

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than arsenious acid. The precipitated sulphuret is more injurious than native orpiment.

SECTION XVII.

CHROMIUM.—VANADIUM.

CHROMIUM.

Chromium[*] was discovered in the year 1797 by Vauquelin in a beautiful red mineral, the native dichromate of oxide of lead. (An. de Ch. xxv. and lxx.) It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron, which occurs abundantly in several parts of the continent, in America, and at Unst in Shetland. (Hibbert.)

Metallic chromium may be obtained by exposing its oxide mixed with charcoal to the most intense heat of a smith's forge; but owing to its strong affinity for oxygen, the reduction is extremely difficult. A better process, that of Vauquelin, is to mix the dry chloride into a paste with oil, place the mass in a crucible lined with charcoal, lute on a cover, and to expose it for an hour to a very strong heat. As thus obtained chromium has a white colour with a shade of yellow, and a distinct metallic lustre. It is a brittle metal, very infusible, and with difficulty attacked by acids, even by the nitro-hydrochloric. Its sp. gravity has been stated at 5.9; but Thomson found it a little above 5. When fused with nitre it is oxidized, and converted into chromic acid. Liebig has obtained the metal in the form of a black powder, which acquires the metallic aspect from pressure, by heating the compound of terchloride of chromium and ammonia to redness, and transmitting over it dry ammoniacal gas: the chlorine unites with the hydrogen of the ammonia, hydrochloric acid and nitrogen gases are evolved, and pulverulent chromium remains. A still more convenient process is to decompose the sesquichloride by heat and ammoniacal gas, in which case, the metal has a chocolate-brown colour. In this finely divided state, it takes fire when heated in the open air. (An. de Ch. et de Ph. xlviii. 297.)

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[*] Χρῶμα, *colour*, from its remarkable tendency to form coloured compounds.

Chromium unites with oxygen in two proportions, forming the green oxide and chromic acid. From the experiments of Berzelius and Thomson the equivalent of chromic acid may be estimated at 52; and as the salts of this acid are isomorphous with the sulphates and seleniates, it is inferred that chromic acid has the same atomic constitution as sulphuric and selenic acids, or consists of one atom of chromium and three atoms of oxygen. Berzelius has moreover remarked, that when the acid is converted into the green oxide of chromium, it parts with exactly half of its oxygen. Hence 24 deducted from 52, leaves 28 as the equivalent of chromium. The composition of its compounds described in this section is as follows:—

	Chromium.					Equiv.	Formulæ.
Sesquioxide	56	2 eq. +	Oxygen	24	3 eq. =	80	$2Cr + 3O$ or $\underline{\dddot{Cr}}$.
Chromic acid	28	1 eq. +	do	24	3 eq. =	52	$Cr + 3O$ or $\dddot{Cr}$.
Sesquichloride	56	2 eq. +	Chlor.	106.26	3 eq. =	162.26	$2Cr + 3Cl$ or Cr^2Cl^3.
Terchloride	28	1 eq. +	do.	106.26	3 eq. =	134.26	$Cr + 3Cl$ or $CrCl^3$.
Sesquifluoride	56	2 eq. +	Fluor.	56.04	3 eq. =	112.04	$2Cr + 3F$ or Cr^2F^3.
Terfluoride	28	1 eq. +	do.	56.04	3 eq. =	84.04	$Cr + 3F$ or CrF^3.
Sesquisulphuret	56	2 eq. +	Sulph.	48.3	3 eq. =	104.3	$2Cr + 3S$ or Cr^2S^3.
Protophosphuret	28	1 eq. +	Phosph.	15.7	1 eq. =	43.7	$Cr + P$ or CrP.

Sesquioxide of Chromium.—This, the only known oxide of chromium, is prepared by dissolving chromate of potassa in water, and mixing it with a solution of nitrate of protoxide of mercury; when an orange-coloured precipitate, chromate of that oxide, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and oxide of chromium.

Oxide of chromium is of a green colour, exceedingly infusible, and suffers no change by heat. It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, or fused with chlorate of potassa, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts. The emerald owes its colour to the presence of this oxide.

Oxide of chromium is a salifiable base, and its salts, which have a green colour, may easily be prepared in the following manner. To a boiling solution of chromate of potassa in water, equal measures of strong hydrochloric acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an excess of pure ammonia into this solution, a pale green bulky hydrate subsides, which consists of one equivalent of the oxide and twenty-six equivalents of water. (Thomson.) The oxide, in this state, is readily dissolved by acids. On expelling the water by heat, the sudden approximation of the particles, which abruptly occurs at a certain temperature, causes such intense evolution of heat that the whole mass becomes vividly incandescent.

The anhydrous oxide is formed when bichromate of potassa is briskly boiled with sugar and a little hydrochloric acid. At first a brown matter falls, consisting of the acid and oxide of chromium; but subsequently the green oxide appears in the form of a finely divided powder. If the bichromate and sugar are employed without hydrochloric acid, the brown matter is the only solid product, and on boiling this compound with a little carbonate of potassa, a greenish-blue carbonate of chromium, of a very fine colour, is obtained. For this mode of preparation I am indebted to my late pupil, Mr. Thomas Thomson, of Clitheroe, near Manchester.

Chromic Acid.—This acid is best prepared by transmitting the gaseous fluoride of chromium into water contained in a vessel of silver or platinum, when by mutual decomposition of the gas and the water, hydrofluoric and chromic acids are generated: the former is then expelled by evaporating the solution to dryness, and the latter in a pure state remains. If the gas is conducted into a silver vessel which is only moistened with water, and the aperture of which is closed by a piece of moist paper, the chromic acid is obtained in the form of acicular crystals of a cinnabar-red colour, which are so voluminous and abundant as to fill the interior of the vessel. Another method of preparing chromic acid has been suggested by M. Arnold Maus, which consists in decomposing a hot concentrated solution of bichromate of potassa by silicated hydrofluoric acid. The chromic acid, after being separated from the sparingly soluble fluoride of silicium and potassium, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water. By this means the last portions of the double salt are rendered insoluble, and the pure chromic acid may be separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into chromate of the green oxide of chromium. When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be safely employed in the first part of the operation, provided care is taken to add a quantity of silicated hydrofluoric acid not quite sufficient for precipitating the whole of the potassa. (Edinburgh Journal of Science, viii. 175.)

This acid was formerly prepared by digesting chromate of baryta or oxide of lead in dilute sulphuric acid, the quantity of the latter being regulated with the view of decomposing the chromate without being in excess. A dark ruby-red solution is thus obtained, which by evaporation yields irregular crystals, and was supposed to contain pure chromic acid; but Gay-Lussac showed that the acid when thus procured is never pure, being intimately combined with sulphuric acid. On endeavouring to expel the latter by heat, the chromic acid itself yields oxygen, and is more or less completely converted into sulphate of the green oxide.

Pure dry chromic acid is black while warm, and of a dark red colour when cold. It is very soluble in water, rendering it red or yellow according to the degree of dilution;—when the solution is concentrated by heat and allowed to cool, it deposites red crystals, which deliquesce readily in the air. In alcohol it is also soluble, but the action of heat or light causes its conversion into the green oxide. Its taste is sour, and with alkalies it acts as a strong acid. It is converted into the green oxide, with evolution of oxygen, by exposure to a strong heat. It yields a chloride when boiled with hydrochloric acid and alcohol, and the direct solar rays have a similar effect when hydrochloric acid is present: the mutual action sets chlorine free, and hence the solution acquires the property of dissolving gold. With sulphurous acid it forms a sulphate of the oxide; and it is more or less completely converted into the oxide by being boiled with sugar, starch, or various other organic principles. It destroys the colour of indigo, and of most vegetable and animal colouring matters; a property advantageously employed in calico-printing, and which manifestly depends on the facility with which it is deprived of oxygen.

Chromic acid is characterized by its colour, and by forming coloured salts with alkaline bases. The most important of these salts is chromate of oxide of lead, which is found native in small quantity, and is easily prepared by mixing chromate of potassa with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to great extent.

When sulphurous acid gas is transmitted into a solution of chromate or bichromate of potassa, a brown precipitate subsides, which was long regarded as a distinct oxide of chromium; but Dr. Thomson has proved that it is the green oxide combined with a little chromic acid. The acid may in a great measure be washed away by means of water, and by ammonia it is entirely removed; but the best mode of separating it, is to dissolve the brown matter with hydrochloric acid, and then precipitate the green oxide by ammonia. The brown compound may be formed by boiling a solution of bichromate of potassa with alcohol; and it is also rapidly generated, when bichromate of potassa is gently boiled with sugar and a very little hydrochloric acid.

Sesquichloride of Chromium.—It is prepared by transmitting dry chlorine gas over a mixture of oxide of chromium and charcoal heated to redness in a tube of porcelain; when the sesquichloride gradually collects as a crystalline sublimate of a peach-purple colour, which in thin layers is transparent, but in thicker masses is opaque. Another method is to evaporate the green solution of this chloride gently to dryness at a temperature of 212°, when a green powder remains, consisting of one eq. of the sesquichloride and three eq. of water ($Cr^2\,Cl^3 + 3\dot{H}$), these elements being exactly in the ratio to form sesquioxide of chromium and hydrochloric acid. On raising the temperature above 212°, no water is lost until it reaches 400°: the powder then begins to swell up from the escape of water, the colour changes from green to the red of peach-blossoms, and pure sesquichloride remains. This part of the process should be conducted in a tube from which air is excluded by a current of dry carbonic acid gas. These phenomena are quoted by Liebig as favouring the notion that the green solution and powder are a hydrochlorate of an oxide and not a chloride with water.

The sesquichloride of chromium dissolves slowly, forming a deep green solution. The same may be prepared by directly dissolving the hydrated oxide in hydrochloric acid; or by digesting chromate of oxide of lead in strong hydrochloric acid, adding a little alcohol from time to time to promote the deoxidation of chromic acid, and then separating the resulting chloride of chromium from that of lead by strong alcohol, which together with any excess of hydrochloric acid is ultimately expelled by evaporating to dryness. Traces of lead which may have been dissolved are easily precipitated by hydrosulphuric acid.

Terchloride of Chromium—This compound is formed by the action of fuming sulphuric acid on a mixture of about equal weights of chromate of oxide of lead and chloride of sodium; or by fusing bichromate of potassa with twice its weight of chloride of sodium, breaking the mass into coarse fragments, and decomposing by fuming sulphuric acid aided by gentle heat. The same change ensues as in the formation of terfluoride of chromium, and a red vapour passes over, which is readily condensed into a heavy volatile liquid of the same colour. It yields abundant red vapours when exposed to the air, and is instantly decomposed by water, yielding a solution of hydrochloric and chromic acids. It was discovered by Unverdorben at the same time with terfluoride of chromium.

Sesquifluoride of Chromium is formed by dissolving the oxide in hydrofluoric acid, and evaporating the solution to dryness, when the sesquifluoride remains as a green crystalline residue, which is soluble in water.

Terfluoride of Chromium.—When a mixture of 3 parts of fluor spar and 4 of chromate of oxide of lead is distilled with 5 parts of fuming or even common sulphuric acid in a leaden or silver retort, a red-coloured gas is disengaged, which acts rapidly upon glass, with deposition of chromic acid and formation of fluosilicic acid gas. It is decomposed by water, and the solution is found to contain a mixture of hydrofluoric and chromic acids. The watery vapour of the atmosphere effects its decomposition; so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid. Its composition is inferred from the products which it forms with water; since

1 eq. terfluoride & 3 eq. water yield 1 eq. chromic & 3 eq. hydrofl. acid.
$Cr+3F$; $3(H+O)$ yield $Cr+3O$ $3(H+F)$.

The red colour of terfluoride of chromium naturally excites the suspicion that the gas itself may consist, not of fluoride of chromium, but of hydrofluoric and chromic acids; and its production by means of *hydrous* sulphuric acid is consistent with this idea. But since the gas may also be formed from fluor spar, chromate of oxide of lead, and *anhydrous* sulphuric acid, it is clear that this view is inadmissible. The changes which accompany the formation of the gas will be apparent on comparing the formulæ of the ingredients used and of the products obtained. Thus,

1eq. chromate ox. lead 4 eq. real sulphuric acid 3 eq. fluor spar
$(Pb+O)+(Cr+3O)$, $4(S+3O)$, $3(Ca+F)$,
yield by mutual reaction
1 eq. terfluoride of chromium; 1 eq. sulphate ox. lead; 3 eq. sulphate of lime.

$Cr+3F$; $\dot{Pb}+\dddot{S}$; $3(\dot{Ca}+\dddot{S})$.

This gas was discovered in the year 1825 by M. Unverdorben. (Ed. Journal of Science, iv. 129.)

Sesquisulphuret of Chromium may be formed by transmitting the vapour of bisulphuret of carbon over oxide of chromium at a white heat; by heating in close vessels an intimate mixture of sulphur and the hydrated oxide; by fusing the oxide with a persulphuret of potassium, and dissolving the soluble parts in water; or by transmitting hydrosulphuric acid gas aided by heat over the sesquichloride of chromium. It cannot be prepared in the moist way. It is of a dark gray colour, and acquires metallic lustre by friction in a mortar. It is readily oxidized when heated in the open air, and is dissolved by nitric or nitro-hydrochloric acid.

Protophosphuret of Chromium.—Rose prepared this compound by acting on the sesquichloride of chromium by phosphuretted hydrogen gas at a red heat. By mutual interchange of elements

1 eq. sesquichloride $2\,Cr+3Cl$ yield 2 eq. phosphuret $2(Cr+P)$
& 1 eq. phosph. hyd. $3H+2P$ & 3 eq. hydrochloric acid $3(H+Cl)$

This phosphuret is black, insoluble in hydrochloric acid, feebly attacked by nitric and nitro-hydrochloric acid, and burns before the blowpipe with a flame of phosphorus.

Another phosphuret of a gray colour may be formed by exposing the phosphate of oxide of chromium to a strong heat in a covered crucible lined with charcoal. Its composition is unknown.

VANADIUM.

Vanadium, so called from *Vanadis*, the name of a Scandinavian Deity, was discovered in the year 1830 by Professor Sefström, of Fahlun, in iron prepared from the iron-ore of Jaberg in Sweden. The state in which it occurs in the ore is unknown; but Sefström separated it from the iron by dissolving the latter in hydrochloric acid, when a black powder came into view containing a small quantity of vanadium, together with iron, copper, cobalt, silica, alumina, and lime. He afterwards found a more abundant source in the slag or cinder formed during the conversion of the cast-iron of Jaberg into malleable iron. Soon after Sefström's discovery, the same metal was found by Mr. Johnston, of Durham, in a mineral from Wanlockhead in Scotland, where it occurs as a vanadiate of oxide of lead. A similar mineral, found at Zimapan in Mexico, was examined in the year 1801 by Professor del Rio, who, in the belief of having discovered a new metal, gave it the name of *Erythronium*, apparently from the red colour of its acid; but as M. Collet Descotils, on being appealed to, declared the mineral to be chromate of lead, del Rio abandoned his own opinion in deference to a higher authority. Thus have three persons noticed the existence of vanadium, without the knowledge of each other's labours; but the merit of being the first discoverer is fairly due to Professor Sefström.*

From the slag above mentioned vanadic acid may be obtained by the following process, contrived by Sefström and improved by Berzelius. The slag in fine powder, mixed with its own weight of nitre and twice its weight of carbonate of potassa, is strongly ignited for the space of one hour. The soluble parts are then removed by boiling water, and the solution, after being filtered and neutralized with colourless nitric acid, is precipitated by chloride of barium or acetate of lead. The precipitate, which consists of vanadiate and phosphate of baryta or oxide of lead, zirconia, alumina, and silicic acid, is decomposed, while still moist, by digestion with strong sulphuric acid; to the deep-red solution alcohol is then added, when by continued digestion ether is disengaged, and all the vanadic acid converted into the salifiable oxide, the solutions of which are blue;—a change effected in order the more completely to remove the vanadic acid from the insoluble matters. The blue liquid is then evaporated, and when it acquires a syrupy consistence, it is mixed in a platinum crucible with a little hydrofluoric acid, and sharply heated in an open fire. By this means the silicic acid, which can only be got rid of in this way, is converted into the gaseous fluoride of silicium, the sulphuric acid expelled, and the oxide reconverted into the acid of vanadium.

The vanadic acid still contains phosphoric acid, alumina, and zirconia. For its further purification it is fused with nitre added in successive small portions, until, on cooling a small quantity, the red tint is found to have disappeared. In this process the acid of the nitre is displaced by the phosphoric and vanadic acids, the object being to cause those acids to unite with potassa without employing an excess of nitre. The vanadiate and phosphate of potassa are then taken up by as small a quantity of water as will suffice, and into the filtered liquid a piece of sal ammoniac, larger than can be dissolved by it, is introduced: as it dissolves, vanadiate of ammonia, insoluble in a saturated solution of sal ammoniac, subsides as a white powder, leaving the phosphoric acid in the liquid. The vanadiate of ammonia should be first washed with a solution of sal ammoniac, and then with alcohol of specific gravity 0.86.

By heating this salt in an open platinum crucible, vanadic acid is obtained; but the temperature ought to be kept below that of redness, and the mass be well stirred until it acquires a dark red colour. Heated in close vessels the vanadiate of ammonia is converted principally into the salifiable oxide; though some of the protoxide and acid are mixed with it. With the zirconia and alumina, left by the water after fusion with nitre, some vanadium remains: it may be extracted by fusion with sulphur and carbonate of potassa, when a double sulphuret of vanadium and potassium is generated, which is soluble in water. On adding sulphuric acid to the solution, sulphuret of vanadium is precipitated.

The preparation of vanadium from the native vanadiate of lead is much less complicated than the process above described. It suffices to dissolve the ore, as Mr. Johnson advises, in nitric acid, and to precipitate the lead by hydrosulphuric acid, which also throws down any arsenic that may be present. As vanadic acid is deoxidized by hydrosulphuric acid, a blue solution is formed; but by evaporating to dryness, the acid is reproduced. The residue is then dissolved by a solution of ammonia, and the vanadiate of ammonia precipitated as before by a piece of sal ammoniac. The vanadic acid is thus separated from arsenic, phosphoric, and hydrochloric acids, with which in the ore of Wanlockhead it is generally associated.

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* Phil. Mag. and Annals, x. 321. An. de Ch. et de Ph. xlvii. 337. Brewster's Journal, v. 318. N. S. Poggendorf's Annalen, xxii. 1.

The attempts of Berzelius to reduce vanadic acid to the metallic state by the agency of hydrogen or charcoal at high temperatures proved unsuccessful, as the protoxide alone was obtained. He procured the metal, however, in the form of heavy black powder, by placing fragment of fused vanadic acid and potassium of equal size in alternate layers in a porcelain crucible, the potassium being in the largest proportion: a cover was then luted on, and heat applied by means of a spirit-lamp. The reduction took place suddenly and with violence; and when the mass had cooled, the potassa and redundant potassium were separated by water. But Berzelius succeeded better by a process similar to that of H. Rose for procuring metallic titanium. The liquid chloride of vanadium is introduced into a glass bulb blown in a barometer tube, and through it is transmitted dry ammoniacal gas until a white saline mass is produced, during the formation of which the gas is rapidly absorbed, and heat disengaged. A spirit-lamp flame is then applied, which expels a quantity of hydrochlorate of ammonia, and metallic vanadium is left adhering to the interior of the bulb. The production of hydrochloric acid is obviously owing to chlorine leaving the vanadium and uniting with the hydrogen of part of the ammonia.

The pulverulent vanadium, produced by means of potassium, has but little of the tenacity and appearance of a metal; though under strong pressure it assumes a lustre like that of graphite. Heated in the open air to commencing redness it takes fire, and is converted into the black protoxide. It conducts electricity however, and is strongly electro-negative in relation to zinc. As procured by Rose's process, the vanadium has a strong metallic lustre and a white colour considerably resembling silver, but still more like molybdenum. It is so extremely brittle that it cannot be removed from the glass bulb without falling into powder. It is not oxidized either by air or water; although by continued exposure to the air its lustre gradually grows weaker, and it acquires a reddish tint. It is not dissolved by boiling sulphuric, hydrochloric, or hydrofluoric acid; but by nitric and nitro-hydrochloric acid it is attacked, and the solution has a beautiful dark blue colour. It is not oxidized by being boiled with caustic potassa, nor by carbonated alkalies at a red heat.

The equivalent of vanadium, according to the analysis of its oxides by Berzelius, is 68.5; and its compounds described in this section are thus constituted:—

	Vanadium.				Equiv.	Formulæ.
Protoxide	68.5	1 eq.+Oxygen	8	1 eq.=	76.5	V+O or $\dot{V}$.
Binoxide	68.5	1 eq.+do.	16	2 eq.=	84.5	V+2O or $\ddot{V}$.
Vanadic acid	68.5	1 eq.+do.	24	3 eq.=	92.5	V+3O or $\dddot{V}$.
Bichloride	68.5	1 eq.+Chlorine	70.84	2 eq.=	139.34	V+2Cl or VCl^2
Terchloride	68.5	1 eq.+do.	106.26	3 eq.=	174.76	V+3Cl or VCl^3
Bibromide	68.5	1 eq.+Bromine	156.8	2 eq =	225.3	V+2Br or VBr^2
Bisulphuret	68.5	1 eq.+Sulphur	32.2	2 eq.=	100.7	V+2S or VS^2.
Tersulphuret	68.5	1 eq.+do.	48.3	3 eq.=	116.8	V+3S or VS^3.

Protoxide.—This compound is readily formed from vanadic acid by the combined agency of heat and charcoal or hydrogen gas. By means of the latter Berzelius found that the reduction is effected as perfectly at a temperature short of ignition, as at the strongest heat of a wind furnace. When prepared from fused vanadic acid, the protoxide retains the crystalline structure of the acid, and has a black colour and a semi-metallic lustre; but it is easily broken down into a fine black powder. When rendered coherent by compression it possesses a property very unusual in oxides, that of conducting electricity, and in relation to zinc of being as strongly electro-negative as silver or copper.

This oxide is very infusible. When heated in open vessels it takes fire and burns like tinder, being converted into the binoxide. On exposure to air and moisture it is slowly oxidized, a process which is best seen by putting it into water, when the liquid gradually acquires a green tint. In both cases the oxygen is derived from the atmosphere. A similar change occurs in acid and alkaline solutions, which, with the exception of nitric acid, do not dissolve it even at a boiling temperature. Heated in nitric acid, oxidation soon ensues with escape of nitric oxide gas, and a blue nitrate of the binoxide of vanadium is generated. The character of an alkaline base seems wholly wanting in the protoxide, and hence Berzelius considers it as a *suboxide*.

Binoxide.—This oxide is best prepared, in the dry way, by heating to full redness an intimate mixture of 10 parts of the protoxide with 12 of vanadic acid in a vessel filled with carbonic acid, or from which combustible matter on the one hand, and oxygen gas on the other, are carefully excluded. From the salts of the binoxide, and especially the sulphate, it is precipitated as a grayish-white hydrate by means of a very slight excess of carbonate of soda. The residual solution is colourless when the process has been properly conducted: it remains blue, from undecomposed salt, if an insufficient quantity of alkali is used; it is brown when the alkaline carbonate is too freely employed, because some of the binoxide is then dissolved by the free alkali; and if the solution contained vanadic acid, its colour after precipitation is green. The presence of the latter is avoided by transmitting hydrosulphuric acid gas into the solution, whereby vanadic acid is effectually converted into the binoxide, but the redundant gas should be expelled by gentle heat before the oxide is precipitated. As the hydrate, while moist, readily absorbs oxygen, and hence acquires a tint of brown, it must be washed and dried without exposure to the air. When thus prepared it retains its gray tint. By exposure to heat in a vessel from which the air is excluded, it gives out water, and acquires all the characters of the oxide prepared in the dry way.

The binoxide of vanadium is a black pulverulent substance, very infusible, insoluble in water, and free from any acid or alkaline reaction. When heated in the open air, it is converted into vanadic acid, and when moist it gradually suffers the same change at ordinary temperatures. It is dissolved by acids more readily as a hydrate than after being heated to redness, and forms salts, most of which have a blue colour, and are more or less soluble in water. They may all be conveniently formed by the direct action of acids on the hydrated oxide. The nitrate may be made by acting on vanadium, or either of its oxides, by nitric acid; the salt, when diluted with water, may be boiled without change; but when evaporated, even spontaneously, the blue colour passes through green into red, owing to the production of vanadic acid. The sulphate is easily prepared by dissolving vanadic acid in warm sulphuric acid diluted with an equal weight of water, decomposing the vanadic acid by hydrosulphuric acid, concentrating the solution in order that the salt may be deposited, and washing away adhering sulphuric acid by means of alcohol. The deoxidation of vanadic acid in the preceding process may also be effected by adding pure oxalic acid as long as carbonic acid gas is evolved.

The salts of the binoxide of vanadium are distinguished by their blue colour, by yielding with the alkalies or their carbonates in very slight excess the hydrated binoxide, which becomes red by oxidation, and by forming with solution of gall-nuts a black compound, a tannate of the binoxide, very similar to ink.

The binoxide is disposed to act the part of an acid by uniting with alkaline bases, with which it forms definite and in some cases crystalline compounds. On digesting the hydrated binoxide in pure potassa or ammonia, combination is readily effected, and a dark brown solution is formed. These compounds, though soluble in water, are very sparingly so in strong and cold alkaline solutions, and may be precipitated by them. Most of the other salts formed by the binoxide and salifiable bases are insoluble in water, and may be formed from the preceding by way of double decomposition.

Vanadic Acid.—When vanadiate of ammonia, prepared as already mentioned, (page 364,) is heated in close vessels, the acid is decomposed by the hydrogen of the ammonia, and binoxide of vanadium is formed, mixed with a little protoxide and undecomposed acid. If the salt is heated in an open vessel, and well stirred, the whole mass acquires a dark red colour, and pure vanadic acid is obtained; but a red heat should be avoided, since fusion would thereby be occasioned, and free exposure of every part to the atmosphere prevented. Its colour in the state of fine powder is a light rust-yellow; but the fused acid is red with a shade of orange, and has a strong lustre. By light transmitted through thin layers it appears yellow. In the fire it is fixed, and is not decomposed by a very strong heat, provided combustible maters are excluded. It fuses at a heat lower than that of redness, and crystallizes readily as it cools. In the act of becoming solid it contracts considerably in volume, and emits so much heat of fluidity that the acid, after ceasing to be luminous, is again rendered incandescent, and remains so until the congelation is complete.

Vanadic acid is tasteless, insoluble in alcohol, and very slightly soluble in water, which takes up rather less than 1-1000th of its weight, acquiring a yellow colour and an acid reaction Heated with combustible matter it is deoxidized, being converted into the protoxide or binoxide, or mixtures of these oxides. In solutions it is deprived of oxygen by all deoxidizing agents, such as alcohol, sugar, and most organic substances, including the oxalic and several vegetable acids, by hydrosulphuric acid and most of the other hydracids, not excepting the hydrochloric, by sulphurous and phosphorous acids, and even by nitrous acid. Like molybdic and tungstic acids, it is disposed to act as a base to such of the stronger acids as do not decompose it, and to form with them definite compounds, which are soluble in water. It unites on this principle with sulphuric and phosphoric acid; and Berzelius has remarked a compound of the phosphoric, silicic, and vanadic acids, a sort of double salt, in which the latter acid is a base to the two former, and which crystallizes in scales: it is formed in Sefström's process for preparing vanadic acid (page 364), and its solubility opposes a great obstacle to the separation of vanadic from silicic acid.

Vanadic acid unites with salifiable bases often in two or more proportions, forming soluble salts with the alkalies, and in general sparingly soluble salts with the other metallic oxides. Those with excess of acid are commonly of a red or orange-red colour. Most of the neutral salts are yellow; but it is singular that the neutral vanadiates of the alkalies, the alkaline earths, and the oxides of lead, zinc, and cadmium may be yellow at one time and colourless at another without suffering any appreciable change in composition. Thus, on neutralizing vanadic acid with ammonia a yellow salt is obtained, the solution of which gradually becomes colourless if kept for some hours, and suffers the same change rapidly when heated. The solution, as it is coloured or colourless, gives a yellow or white residue by evaporation, and a yellow or white precipitate with a salt of baryta or oxide of lead. These changes appear to be of the same kind as those already noticed in the description of phosphoric acid.

Vanadic acid unites in different proportions with binoxide of vanadium, and forms compounds which are soluble in pure water but sparingly so in saline solutions, and which are purple, green, yellow, or orange, according as the acid is in a smaller or larger proportion. They are best formed by exposing the hydrated binoxide to the atmosphere, when these different colours successively appear, as a gradually increasing quantity of the acid is generated.

Vanadic acid is distinguished from all other acids except the chromic by its colour, and from this acid by the action of deoxidizing substances, which give a blue solution with the former and a green with the latter. (Page 361.) When heated with borax in the reducing flame of the blowpipe, both of the acids yield a green glass; but in the oxidizing flame the bead becomes yellow if vanadium is present, while the green colour produced by chromium is permanent.

Chlorides.—The *bichloride* is prepared by digesting a mixture of the vanadic and hydrochloric acids, deoxidizing any undecomposed vanadic acid by hydrosulphuric acid, and evaporating the solution to dryness. A brown residue is obtained, which yields a blue solution with water, part being left as an insoluble subsalt. It may also be generated by acting directly on the ignited binoxide with strong hydrochloric acid. As thus obtained its solution is brown instead of blue, though in composition it seems identical with the preceding.

The *terchloride* may be formed by transmitting a current of dry chlorine gas over a mixture of protoxide of vanadium and charcoal heated to low redness, when the terchloride passes over in vapour, and condenses in the form of a yellow liquid, from which free chlorine may be removed by a current of dry air. It is converted by water into hydrochloric and vanadic acid, and atmospheric humidity produces the same change, which is indicated by the escape of red fumes.

A *bibromide* of vanadium may be formed in the same manner as the bichloride, substituting the hydrobromic for hydrochloric acid. Similar compounds may be procured with iodine, fluorine, and cyanogen, by dissolving binoxide of vanadium in hydriodic, hydrofluoric, and hydrocyanic acid.

Sulphurets.—When the binoxide of vanadium is heated to redness in a current of hydrosulphuric acid gas, it is converted into protoxide, and both water and sulphur are obtained: on continuing the process the protoxide is decomposed, hydrogen gas and water pass over, and *bisulphuret* of vanadium is generated. This compound may also be procured by mixing hydrosulphate of ammonia with a salt of the binoxide of vanadium until the precipitate at first formed is redissolved, and then decomposing the deep purple-coloured solution by sulphuric or hydrochloric acid. The bisulphuret of a brown colour subsides, which becomes black when it is dried. It is unchanged at common temperatures by exposure to the air, but takes fire when heated. In the hydrated state it is dissolved by alkalies and alkaline sulphurets; but it is insoluble in acids, with the exception of the nitric and nitro-hydrochloric, by which it is converted into sulphate of the binoxide.

When hydrosulphuric acid gas is transmitted through an aqueous solution of vanadic acid, a grayish-brown precipitate is formed, consisting of hydrated binoxide of vanadium mixed mechanically with sulphur. But if a solution of vanadic acid in hydrosulphate of ammonia is acidulated by hydrochloric or sulphuric acid, the hydrated *tersulphuret* of vanadium subsides. Its colour is of a much lighter brown than the bisulphuret, becomes almost black in drying, and is resolved by a red heat in close vessels into the bisulphuret, with loss of water and sulphur. It is soluble in alkalies and alkaline sulphurets, and is oxidized by nitric acid.

The phosphuret of vanadium, of a leaden-gray colour, may be formed by exposing to a white heat phosphate of the binoxide of vanadium mixed with a small quantity of sugar.

SECTION XVIII.

MOLYBDENUM.—TUNGSTEN.—COLUMBIUM.

MOLYBDENUM.

When native sulphuret of molybdenum, in fine powder, is digested in nitro-hydrochloric acid until the ore is completely decomposed, and the residue is briskly heated in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas while strongly heated in a tube of porcelain. (Berzelius.) The sulphuret, which was long mistaken for graphite, was distinguished in 1778 by Scheele; but the metal was first obtained in a separate state by Hjelm. It likewise occurs in nature in the form of molybdate of oxide of lead.

Molybdenum is a brittle metal, of a white colour, and so very infusible, that hitherto it has only been obtained in a state of semi-fusion. In this form it has a specific gravity varying between 8.615 and 8.636. When heated in open vessels it absorbs oxygen, and is converted into *molybdic acid;* and the same compound is generated by the action of chlorine or nitro-hydrochloric acid. It has three degrees of oxidation, forming two oxides and one acid, from the composition of which Berzelius estimates the equivalent of molybdenum at 47.7. The composition of its compounds described in this section is as follows:—

	Molybdenum.				Equiv.	Formulæ.
Protoxide	47.7	1 eq.+Oxygen	8	1 eq.=	55.7	Mo+O or $\dot{Mo}$.
Binoxide	47.7	1 eq.+do.	16	2 eq.=	63.7	Mo+2O or $\ddot{Mo}$.
Molybdic acid	47.7	1 eq.+do.	24	3 eq.=	71.7	Mo+3O or $\dddot{Mo}$.
Protochloride	47.7	1 eq.+Chlorine	35.42	1 eq.=	83.12	Mo+Cl or MoCl.
Bichloride	47.7	1 eq.+do.	70.84	2 eq.=	118.54	Mo+2Cl or $MoCl^2$.
Terchloride	47.7	1 eq.+do.	106.26	3 eq.=	153.96	Mo+3Cl or $MoCl^3$.
Bisulphuret	47.7	1 eq.+Sulphur	32.2	2 eq.=	79.9	Mo+2S or MoS^2.
Tersulphuret	47.7	1 eq.+do.	48.3	3 eq.=	96	Mo+3S or MoS^3.
Persulphuret	47.7	1 eq.+do.	64.4	4 eq.=	112.1	Mo+4S or MoS^4.

Protoxide of Molybdenum. On dissolving molybdate of potassa or soda in a small quantity of water, adding hydrochloric acid until the molybdic acid at first thrown down is redissolved, and digesting with a piece of pure metallic zinc, the latter deoxidizes the molybdic acid, the liquid changes to blue, red, and black, and then contains chloride of zinc and protochloride of molybdenum. From the black solution pure potassa throws down the protoxide of molybdenum as a black hydrate, an excess of the alkali being used in order to hold the zinc in solution. The hydrate is washed with the least possible exposure to the air, and dried in vacuo by sulphuric acid. When heated to low redness in the open air, it takes fire and is converted into the binoxide; but if not exposed to the air, it becomes incandescent at the moment of losing its water, like hydrated oxide of chromium. The anhydrous oxide is black and insoluble in acids; but in the state of hydrate acids dissolve it. The recently precipitated hydrate is soluble in the cold by carbonate of ammonia, but in none of the other alkalies.

Binoxide of Molybdenum.—It is obtained as a deep brown anhydrous powder by mixing molybdate of soda with half its weight of sal ammoniac in fine powder, projecting the mixture into a red-hot crucible which is to be instantly covered, and the heat continued until vapours of sal ammoniac cease to appear. In this process chloride of sodium is generated, and molybdic acid is reduced by the ammonia to the state of binoxide: by adding water to the mass when cold, chloride of sodium is dissolved, and the dark brown, nearly black, binoxide left. The hydrate, of a rust-brown colour, may be formed by digesting molybdenum in powder with molybdic acid dissolved in hydrochloric acid, until the liquid acquires a deep red colour, and then adding ammonia; or by adding ammonia to a solution of the bichloride; or digesting with metallic copper a solution of molybdic in hydrochloric acid until a deep red solution is formed, and employing an excess of ammonia in order to keep oxide of copper in solution.

The anhydrous binoxide is insoluble in acids and is changed into molybdic acid by strong nitric acid. The hydrate is very like hydrated peroxide of iron, reddens litmus paper when placed on it, is dissolved by acids with which it forms red salts, is insoluble in the alkalies, but dissolves in alkaline carbonates. It is soluble, though sparingly, in pure water, so that it should be washed after precipitation by a solution of sal ammoniac, which salt is afterwards removed by alcohol. On exposure to the air the hydrate absorbs oxygen and becomes blue at its surface: this blue compound is more soluble in water than the hydrate, and was supposed by Buchholz to be a distinct acid, which he termed *molybdous acid;* but Berzelius has shown that it is a bimolybdate of the binoxide. (Berzelius.)

Molybdic Acid.—When sulphuret of molybdenum is roasted in an open crucible kept at a low red heat, and constantly stirred until sulphurous acid ceases to escape, a dirty yellow powder is left, which contains impure molybdic acid. The acid is taken up by ammonia and the filtered solution evaporated to dryness; it is again taken up by water, a little ammonia being added, and filtered; and it is then purified by crystallization. On heating gently in an open platinum crucible, taking care to prevent fusion, the ammonia is expelled, and pure acid remains. It is also obtained by oxidizing the binoxide with nitric acid.

Molybdic acid, as thus formed, is a white powder, of sp. gravity 3.49, fusible by a red heat into a yellow liquid, which bears a strong red heat in closed vessels without subliming, but in an open crucible rises with the current of air, and collects on cold surfaces in colourless crystalline scales. It requires 570 times its weight of water for solution, which nevertheless has an acid reaction. It is soluble in the alkalies, forming colourless molybdates, from which molybdic acid is precipitated by the stronger acids, though an excess of the acids dissolves it; but after exposure to a red heat it is insoluble in acids.

Chlorides.—Berzelius has described three chlorides of molybdenum which are analogous in composition to the oxides. The *protochloride* is formed by dissolving the hydrated protoxide in hydrochloric acid, forming a deep nearly black coloured solution, which leaves a black viscid mass by evaporation.

The *bichloride* is obtained as above mentioned, and yields a red solution. It is obtained in the anhydrous state by gently heating molybdenum in powder in dry chlorine gas, atmospheric air being excluded. The metal takes fire at its surface, but it is soon extinguished, after which the chlorine is replaced by a red vapour of such intensity that it is completely opaque in a vessel ¾ of an inch in diameter: this vapour condenses in the cooler parts of the apparatus in brilliant black crystals just like those of iodine, which are very fusible, and sublime at a gentle heat. Exposed to dry oxygen gas, it is transformed gradually into terchloride of molybdenum and molybdic acid; so that

3 eq. bichloride and 3 eq. oxygen yield 2 eq. terchloride and 1 eq. molybdic acid.
$3(\mathrm{Mo}+2\mathrm{Cl})$ $3\mathrm{O}$ $2(\mathrm{Mo}+3\mathrm{Cl})$ $\mathrm{Mo}+3\mathrm{O}$.

With water the bichloride acts violently from the intense heat evolved, and the whole is dissolved.

The *terchloride* is obtained in solution by dissolving molybdic in hydrochloric acid; and in the anhydrous state by heating molybdic acid in a current of dry chlorine gas. It is white with a shade of yellow, sublimes at a heat short of redness and condenses in crystalline scales, and is soluble in water and alcohol.

Sulphurets.—Molybdenum combines with sulphur in three proportions. The lowest grade is the *bisulphuret*, which is the most common ore of molybdenum and is usually associated with ores of tin, has a lead-gray colour and metallic lustre resembling graphite, for which it was formerly mistaken. Its density varies from 4.138 to 4.569. It bears a strong heat in close vessels without change or fusion; but it is oxidized by nitric acid or by the joint action of heat and air.

The *tersulphuret* is obtained by saturating molybdate of potassa, soda, or ammonia with hydrosulphuric acid gas, and adding hydrochloric acid, when the tersulphuret falls of a deep brown colour, which becomes black on drying. It is partially oxidized when dried in the air. By heat in close vessels it is changed into the bisulphuret with loss of sulphur.

The *persulphuret* is made by boiling the sulphur-salt formed of tersulphuret of molybdenum and sulphuret of potassium for a long time with the bisulphuret of molybdenum, when a precipitate collects which is to be well washed with cold water. It is a sulphur-salt composed of persulphuret of molybdenum and sulphuret of potassium, which forms with boiling water a deep red solution, from which on the addition of hydrochloric acid the persulphuret subsides.

TUNGSTEN.

It derives its name from the Swedish words *Tung Sten*, *heavy stone*, from the density of its ores; and it is called wolfram from the mineral of that name, which is a tungstate of the oxides of iron and manganese. This metal may be procured in the metallic state by exposing tungstic acid to the action of charcoal or dry hydrogen gas at a red heat; but though the reduction is easily effected, an exceedingly intense temperature is required for fusing the metal. Tungsten has a grayish-white colour, and considerable lustre. It is brittle, nearly as hard as steel, and less fusible than manganese. Its specific gravity is near 17.6. When heated to redness in the open air it takes fire, and is converted into tungstic acid; and it undergoes the same change by the action of nitric acid. Digested with a concentrated solution of pure potassa, it is dissolved with disengagement of hydrogen gas, and tungstate of potassa is generated.

Chemists are acquainted with two compounds of this metal and oxygen, namely, the *dark brown oxide* and the *yellow acid of tungsten;* and according to the analysis of Berzelius, (An. de Ch. et de Ph. xvii.) the oxygen of the former is to that of the latter in the ratio of two to three. From the composition of the latter, and assuming that it contains three atoms of oxygen, the equivalent of tungsten is 99.7. Its compounds described in this section are thus constituted:—

	Tungsten.			Equiv.	Formulæ.
Binoxide	99.7	1 eq.+Oxygen	16	2 eq.=115.7	$W+2O$ or $\ddot{W}$.
Tungstic acid	99.7	1 eq.+ditto	24	3 eq.=123.7	$W+3O$ or $\dddot{W}$.
Bichloride	99.7	1 eq.+Chlor.	70.84	2 eq.=170.54	$W+2Cl$ or WCl^2.
Terchloride	99.7	1 eq.+ditto	106.26	3 eq.=205.96	$W+3Cl$ or WCl^3.
Bisulphuret	99.7	1 eq.+Sulph.	32.2	2 eq.=131.9	$W+2S$ or WS^2
Tersulphuret	99.7	1 eq.+ditto	48.3	3 eq.=483	$W+3S$ or WS^3

Binoxide.—This oxide is formed by the action of hydrogen gas on tungstic acid at a low red heat; but the best mode of procuring it both pure and in quantity, is that recommended by Wöhler. (Quarterly Journal of Science, xx. 177(. This process consists in mixing wolfram in fine powder with twice its weight of carbonate of potassa, and fusing the mixture in a platinum crucible. The resulting tungstate of potassa is dissolved in hot water, mixed with about half its weight of hydrochlorate of ammonia in solution, evaporated to dryness, and exposed in a Hessian crucible to a red heat. The mass is well washed with boiling water, and the insoluble matter digested in dilute potassa to remove any tungstic acid. The residue is oxide of tungsten. It appears that in this process the tungstate of potassa and hydrochlorate of ammonia mutually decompose each other, so that the dry mass consists of chloride of potassium and tungstate of ammonia. The elements of the latter react on each other at a red heat, giving rise to water, nitrogen gas, and binoxide of tungsten; and this compound is protected from oxidation by the fused chloride of potassium with which it is enveloped. This oxide is also formed by putting tungstic acid in contact with zinc in dilute hydrochloric acid. The tungstic acid first becomes blue and then assumes a copper colour; but the oxide in this state can with difficulty be preserved, as by exposure to the air, and even under the surface of water, it absorbs oxygen, and is reconverted into tungstic acid.

Binoxide of tungsten, when prepared by means of hydrogen gas, has a brown colour, and when polished acquires the colour of copper; but when procured by Wöhler's process, it is nearly black. It does not unite, so far as is known, with acids; and when heated to near redness, it takes fire and yields tungstic acid.

Tungstic Acid.—A convenient method of preparing tungstic acid is by digesting native tungstate of lime, very finely levigated, in nitric acid; by which means nitrate of lime is formed, and tungstic acid separated in the form of a yellow powder. Long digestion is required before all the lime is removed; but the process is facilitated by acting upon the mineral alternately by nitric acid and ammonia. The tungstic acid is dissolved readily by that alkali, and may be obtained in a separate state by heating the tungstate of ammonia to redness. Tungstic acid may also be prepared by the action of hydrochloric acid on wolfram. It is also obtained by heating the brown oxide to redness in open vessels.

Tungstic acid is of a yellow colour, is insoluble in water, and has no action on litmus paper. With alkaline bases it forms salts called *tungstates*, which are decomposed by the stronger acids, the tungstic acid in general falling combined with the acid by which it is precipitated. When strongly heated in open vessels, it acquires a green colour, and becomes blue when exposed to the action of hydrogen gas at a temperature of 500° or 600° F. The blue compound, according to Berzelius, is a tungstate of the binoxide of tungsten; and the green colour is probably produced by an admixture of this compound with the yellow acid.

Chlorides of Tungsten.—According to Wöhler, tungsten and chlorine united in three proportions. When metallic tungsten is heated in chlorine gas, it takes fire, and yields the *bichloride*. The compound appears in the form of delicate needles, of a deep red colour, resembling wool, but more frequently as a deep red fused mass which has the brilliant fracture of cinnabar. When heated, it fuses, boils, and yields a red vapour. By water it is changed into hydrochloric acid and binoxide of tungsten. It is entirely dissolved by solution of pure potassa and disengagement of hydrogen gas, yielding tungstate of potassa and chloride of potassium. A similar change is produced by ammonia, except that some binoxide of tungsten is left undissolved.

The *terchloride* is generated by heating the binoxide of tungsten in chlorine gas. The action is attended with the appearance of combustion, dense fumes arise, and a thick sublimate is obtained in the form of white scales, like native boracic acid. It is volatile at a low temperature without previous fusion. It is converted by the action of water into tungstic and hydrochloric acids.

Another chloride has been described by Wöhler. It is formed at the same time as the first; and though it is converted into hydrochloric and tungstic acids by the action of water, and would thus seem identical with the terchloride in the proportion of its elements, its other properties are nevertheless different. It is the most beautiful of all these compounds, existing in long transparent crystals of a fine red colour. It is very fusible and volatile, and its vapour is red like that of nitrous acid. The difference betweeen this compound and the chloride first described has not yet been discovered.

Sulphurets of Tungsten.—The *bisulphuret* is obtained as a black powder by transmitting hydrosulphuric acid gas, or the vapour of sulphur, over tungstic acid heated to whiteness in a tube of porcelain. The tersulphuret is prepared by dissolving tungstic acid in a solution of sulphuret of potassium or hydrosulphate of ammonia, and adding an excess of hydrosulphuric acid. It falls as a brown precipitate, which becomes black in drying. It is soluble to a certain extent in water which is free from saline matter.

COLUMBIUM.

This metal was discovered in 1801 by Mr. Hatchett, who detected it in a black mineral belonging to the British Museum, supposed to have come from Massachusetts in North America; and from this circumstance applied to it the name of *columbium*. About two years after, M. Ekeberg, a Swedish chemist, extracted the same substance from *tantalite* and *yttro-tantalite;* and, on the supposition of its being different from columbium, described it under the name of *tantalum*. The identity of these metals, however, was established in the year 1809 by Dr. Wollaston.

Columbic acid is with difficulty reduced to the metallic state by the action of heat and charcoal; but Berzelius succeded in obtaining this metal by the same process which he employed in the preparation of zirconium and silicium; namely, by heating potassium with the double fluoride of potassium and columbium. On washing the reduced mass with hot water, in order to remove the fluoride of potassium, columbium is left in the form of a black powder. In this state it does not conduct electricity; but in a denser state it is a perfect conductor. By pressure it acquires metallic lustre, and has an iron-gray colour. It is not fusible at the temperature at which glass is fused. When heated in the open air, it takes fire considerably below the temperature of ignition, and glows with a vivid light, yielding columbic acid. It is scarcely at all acted on by the sulphuric, hydrochloric, or nitro-hydrochloric acid; whereas it is dissolved with heat and disengagement of hydrogen gas by hydrofluoric acid, and still more easily by a mixture of nitric and hydrofluoric acids. It is also converted into columbic acid by fusion with hydrate of potassa, the hydrogen gas of the water being evolved.

From the experiments of Berzelius on the composition of the oxide and acid of columbium, its equivalent may be estimated at 185. Its compounds described in this section are thus constituted:—

	Columbium.		Equiv.	Formulæ.
Binoxide	185 1 eq.+Oxygen	16	2 eq.=201	$Ta+2O$ or $\ddot{Ta}$.
Columbic acid	185 1 eq.+ do.	24	3 eq.=209	$Ta+3O$ or $\dddot{Ta}$.
Terchloride	185 1 eq.+Chlorine	106.26	3 eq.=291.26	$Ta+3Cl$ or $TaCl^3$.
Terfluoride	185 1 eq.+Fluorine	56.04	3 eq.=241.04	$Ta+3F$ or TaF^3.
Sulphuret	Composition uncertain.			

Binoxide of Columbium.—It is generated by placing columbic acid in a crucible lined with charcoal, luting carefully to exclude atmospheric air, and exposing it for an hour and a half to intense heat. The acid, where in direct contact with charcoal, is entirely reduced; but the film of metal is very thin. The interior portions are pure binoxide of a dark gray colour, very hard and coherent. When reduced to powder its colour is dark brown. It is not attacked by any acid, even by the nitro-hydrofluoric; but it is converted into columbic acid either by fusion with hydrate of potassa, or deflagration with nitre. When heated to low redness, it takes fire and glows, yielding a light gray powder; but in this way it is never completely oxidized. Berzelius states that this oxide, in union with protoxide of iron and a little protoxide of manganese, occurs at Kimito in Finland, and may be distinguished from the other ores of columbium by yielding a chestnut-brown powder.

Columbic Acid.—Columbium exists in most of its ores as an acid, united either with the oxides of iron and manganese, as in tantalite, or with the earth yttria, as in the yttro-tantalite. This acid is obtained by fusing its ore with three or four times its weight of carbonate of potassa, when a soluble columbate of that alkali results, from which columbic acid is precipitated as a white hydrate by acids. Berzelius also prepares it by fusion with bisulphate of potassa.

Hydrated columbic acid is tasteless and insoluble in water; but when placed on moistened litmus paper, it communicates a red tinge. It is dissolved by the sulphuric, hydrochloric, and some vegetable acids; but it does not diminish their acidity, or appear to form definite compounds with them. With alkalies it unites readily; and though it does not neutralize their properties completely, crystallized salts may be obtained by evaporation. When the hydrated acid is heated to redness, water is expelled, and the anhydrous columbic acid remains. In this state it is attacked by alkalies only.

Terchloride of Columbium.—When columbium is heated in chlorine gas, it takes fire and burns actively, yielding a yellow vapour, which condenses in the cold parts of the apparatus in the form of a white powder with a tint of yellow. Its texture is not in the least crystalline. By contact with water, it is converted, with a hissing noise and increase of temperature, into columbic and hydrochloric acids.

Terfluoride of Columbium.—Hydrofluoric acid takes up hydrated columbic acid, and forms with it a compound of terfluoride of columbium and hydrofluoric acid, which, by evaporation at 76°, is deposited in crystals, which are soluble in water and effervesce in the air. By gently evaporating the solution, an uncrystalline mass, white and opaque, is left, which Berzelius considers to be the terfluoride of columbium. By water part of it is converted into columbic and hydrofluoric acids, the latter soluble and the former insoluble; but both of these acids retain some terfluoride in combination.

Sulphuret of Columbium.—This compound, first prepared by Rose, is generated, with the phenomena of combustion, when columbium is heated to commencing redness in the vapour of sulphur; or by transmitting the vapour of bisulphuret of carbon over columbic acid in a porcelain tube at a white heat, carbonic oxide being also evolved.

SECTION XIX.

ANTIMONY.

Antimony was first made known as a metal in the 15th century by Basil Valentine, and is said to derive its name (*antimoine, anti-monk*) from having proved fatal to some monks to whom it was given as a medicine. It sometimes occurs native; but its only ore which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This ore, the *stibium* of the ancients, was long regarded as the metal itself, and was called *antimony*, or *crude antimony*; while the pure metal was termed the *regulus of antimony*.

Metallic antimony may be obtained either by heating the native sulphuret in a covered crucible with half its weight of iron filings; or by mixing it with two-thirds of its weight of cream of tartar and one-third of nitre, and throwing the mixture, in small successive portions, into a red-hot crucible. By the first process the sulphur unites with iron, and in the second it is expelled in the form of sulphurous acid; while the fused antimony, which in both cases collects in the bottom of the crucible, may be drawn off and received in moulds. The antimony, thus obtained, is not absolutely pure; and, therefore, for chemical purposes, should be procured by heating the oxide with an equal weight of cream of tartar.

Antimony is a brittle metal, of a white colour running into bluish-gray, and is possessed of considerable lustre. Its density is nearly 6.7. At 810° it fuses, and on cooling acquires a highly lamellated texture, and sometimes yields crystals: like arsenic, but unlike most other metals, its primary form is a rhombohedron. It has the character of being a volatile metal; but Thenard found that it bears an intense white heat without subliming, provided atmospheric air be perfectly excluded, and no gaseous matters, such as carbonic acid or watery vapour, be disengaged during the process. Its surface tarnishes by exposure to the atmosphere; and by the continued action of air and moisture, a dark matter is formed, which Berzelius regards as a definite compound. It appears, however, to be merely a mixture of the sesquioxide and metallic antimony. Heated to a white or even full red heat in a covered crucible, and then suddenly exposed to the air, it inflames, and burns with a white light. During the combustion a white vapour rises, which condenses on cool surfaces, frequently in the form of small shining needles of silvery whiteness. These crystals were formerly called *argentine flowers of antimony*, and in chemical works are generally described as antimonious acid; but they are correctly considered by Berzelius as the sesquioxide.

From the experiments of Berzelius on the composition of the oxide and acids of antimony (An. de Ch. et de Ph. xvii.), the equivalent of that metal may be estimated at 64.6. The composition of its compounds described in this section is as follows:—

	Two eq. Antimony.		Equiv.	Formulæ.
Sesquioxide	129.2 + Oxygen	24	3 eq. = 153.2	2Sb + 3O or $\underline{\overset{\cdots}{Sb}}$.
Antimonious acid	129.2 + do.	32	4 eq. = 161.2	2Sb + 4O or $\underline{\overset{\cdot\cdot\cdot\cdot}{Sb}}$.
Antimonic acid	129.2 + do.	40	5 eq. = 169.2	2Sb + 5O or $\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{Sb}}$.
Sesquichloride	129.2 + Chlorine	106.26	3 eq. = 235.46	2Sb + 3Cl or Sb^2Cl
Bichloride	129.2 + do.	141.68	4 eq. = 270.88	2Sb + 4Cl. or Sb^2Cl^4.
Perchloride	129.2 + do.	177.1	5 eq. = 306.3	2Sb + 5Cl or Sb^2Cl^5.
Bromide	Composition uncertain.			
Sesquisulphuret	129.2 + Sulphur	48.3	3 eq. = 177.5	2Sb + 3S or Sb^2S^3.
Bisulphuret	129.2 + do.	64.4	4 eq. = 193.6	2Sb + 4S or Sb^2S^4.
Persulphuret.	129.2 + do.	80.5	5 eq. = 209.7	2Sb + 5S or Sb^2S^5.
Oxy-sulph. of antim.	Sesquisulph. Sesquioxide.	355 153.2	2 eq. 1 eq. = 508.2	$2Sb^2S^3 + \underline{\overset{\cdots}{Sb}}$.

Sesquioxide.—When sesquichloride of antimony, made by boiling the native sulphuret in hydrochloric acid (page 258), is poured into water, a white curdy precipitate subsides, formerly called *powder of Algaroth*, which consists of sesquioxide of antimony combined with a little hydrochloric acid, or more probably with undecomposed chloride. On decomposing the latter by digestion with carbonate of potassa and then washing with water, the sesquioxide is obtained in a state of purity. It may also be procured by adding carbonate of potassa or soda to a solution of tartar emetic, and by sublimation during the combustion of antimony. When slowly sublimed it condenses in fine needles of silvery whiteness. It occurs as a mineral, the oxide of antimony of mineralogists, the primary form of which is a right rhombic prism, isomorphous with the crystals of arsenious acid lately observed by Wöhler. (Page 354.)

Sesquioxide of antimony, when prepared in the moist way, is a white powder with a somewhat dirty appearance. When heated it acquires a yellow tint, and at a dull red heat in close vessels it is fused, yielding a yellow fluid, which becomes an opaque grayish crystalline mass on cooling. Its sp. gravity is 5.566. It is very volatile, and if protected from atmospheric air may be sublimed without change. When heated in open vessels it absorbs oxygen; and when the temperature is suddenly raised, and the oxide is porous, it takes fire and burns. In both cases antimonious acid is generated. It is the only oxide of antimony which forms regular salts with acids, and is the base of the medicinal preparation *tartar emetic*, the tartrate of antimony and potassa. Most of its salts, however, are either insoluble in water, or, like chloride of antimony, are decomposed by it, owing to the affinity of that fluid for the acid being greater than that of the acid for oxide of antimony. This oxide is, therefore, a feeble base; and, indeed, possesses the property of uniting with alkalies. To the foregoing remark, however, tartrate of antimony and potassa is an exception; for it dissolves readily in water without change. By excess of tartaric or hydrochloric acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by hydrosulphuric acid. This gas occasions an orange-coloured precipitate, hydrated sesquisulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of hydrosulphuric acid gas by hot hydrochloric acid, forming a solution from which the white oxy-chloride (*powder of Algaroth*) is precipitated by water.

In trying the effect of reagents on solutions of sesquioxide of antimony, it is convenient to employ tartar emetic, from its property of dissolving in pure water without decomposition. From a solution of this salt, when moderately concentrated, a little pure potassa throws down the oxide, but excess of the alkali dissolves the precipitate. The oxide is more perfectly separated by alkaline carbonates. Lime-water causes a white precipitate, a mixed tartrate of lime and sesquioxide of antimony; and earthy and metallic salts decompose tartar emetic by forming, like lime, sparingly soluble compounds with tartaric acid. Decomposition is also occasioned by most acids, which throw down a sparingly soluble salt of antimony and cream of tartar; and a recently made, pretty strong, infusion of gall-nuts gives a yellowish-white precipitate, which consists of tannin and sesquioxide of antimony. But these appearances are by no means to be relied on as tests of the presence of antimony: a mixture of other substances might be similarly influenced by the same reagents; in a moderately dilute solution of tartar emetic most of them produce no effect whatever; and the too free addition of a pure alkali or of an acid, even to a strong solution, may altogether prevent that precipitate from forming, which a smaller quantity of the same reagents would have produced. The only certain method of bringing the antimony into view, even in a very weak solution, is to acidulate with tartaric acid, and then transmit through the liquid a current of hydrosulphuric acid gas. The hydrated sesquisulphuret of antimony, of a characteristic orange-red colour, is immediately formed.

The detection of antimony in mixed fluids, as when tartar emetic is mixed with articles of food, is conducted in the following manner.—The substances are first digested in water acidulated with about a drachm of hydrochloric and tartaric acids, which coagulate some organic matters, and give complete solubility to the sesquioxide of antimony. Through the filtered liquid, hydrosulphuric acid is then transmitted, when the orange-red sesquisulphuret of antimony subsides, which preserves its characteristic tint even when deposited from coloured solutions, and may be further recognized by solution in hot hydrochloric acid and precipitation by water. The metal itself may in general be obtained by placing the dry sulphuret in a glass tube, transmitting through it a current of hydrogen gas, and then, when all the atmospheric air is displaced, heating the sulphuret by the flame of a spirit-lamp. The sulphur is carried off in the form of hydrosulphuric acid gas, and the metallic antimony, recognizable by its lustre, remains. The metal is principally found where the sulphuret lay; but if the current of gas during the reduction happen to be rapid, it causes mechanically a spurious sublimation of antimony, which lines part of the tube with a thin film of metal. When much organic matter is mixed with the sulphuret, the metal is sometimes indistinctly seen. In that case it should be dissolved in a few drops of nitro-hydrochloric acid with heat, and be precipitated by water: it may then be redissolved by tartaric acid, and again precipitated with its characteristic tint by hydrosulphuric acid. Orfila recommends that the metal should be obtained from the sulphuret by fusion with black flux; but I have elsewhere shown this process to be very precarious, and my opinion is supported by the experience of Dr. Christison. (Treatise on Poisons, 2nd Ed. 429.)

Antimonious Acid.—When metallic antimony is digested in strong nitric acid, the metal is oxidized at the expense of the acid, and hydrated antimonic acid is formed; and on exposing this substance to a red heat, it gives out water and oxygen gas, and is converted into antimonious acid. It is also generated when the oxide is exposed to heat in open vessels. Thus, on heating sulphuret of antimony with free exposure to the air, sulphurous acid and sesquioxide of antimony are generated; but on continuing the roasting until all the sulphur is burned, the oxide gradually absorbs oxygen and passes into antimonious acid. Hence this acid is formed in the process of preparing the *Pulvis Antimonialis* of the Pharmacopœia. Antimonious acid is white while cold, but acquires a yellow tint when heated, is very infusible, and fixed in the fire, two characters by which it is readily distinguished from the oxide. It is insoluble in water, and likewise in acids after being heated to redness. It combines in definite proportions with alkalies, and its salts are called *antimonites*. Antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by hydrochloric and tartaric acids, though without appearing to form with them definite compounds.

Antimonic Acid, sometimes called *peroxide* of antimony, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitro-hydrochloric acid, concentrating by heat to expel excess of acid, and throwing the solution into water. When recently precipitated it reddens litmus paper, and may then be dissolved in water by means of hydrochloric or tartaric acid. It does not enter into definite combination with acids, but with alkalies forms salts, which are called *antimoniates*. When hydrated antimonic acid is exposed to a temperature of 500° or 600° F. the water is evolved, and the anhydrous acid of a yellow colour remains. In this state it resists the action of acids. When exposed to a red heat, it parts with oxygen, and is converted into antimonious acid.

Chlorides of Antimony.—When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and the *sesquichloride* of antimony is generated. The same compound may be formed by distilling a mixture of antimony with about twice and a half its weight of corrosive sublimate, when the volatile sesquichloride of antimony passes over into the recipient, and metallic mercury remains in the retort. At common temperatures it is a soft solid, thence called *butter* of antimony, which is liquefied by gentle heat, and crystallizes on cooling. It deliquesces on exposure to the air; and when mixed with water, hydrochloric acid and sesquioxide are generated, and the latter, combined with a little undecomposed chloride, subsides.

The *bichloride* of antimony is formed by acting on hydrated antimonious by hydrochloric acid, when a solution is formed, which appears to be a compound of bichloride of antimony and hydrochloric acid. It possesses little permanence, and on the addition of water, antimonious acid subsides, and hydrochloric acid remains in solution.

The *perchloride* is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air. Mixed with water, it is converted into hydrochloric acid, and hydrated antimonic acid which subsides. (Rose, in the Annals of Philosophy, N. S. x.)

Bromide of Antimony.—The union of bromine and antimony is attended with disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic. It is solid at common temperatures, is fused at 206°, and boils at 518° F. It is colourless and crystallizes in needles; it attracts moisture from the air, and is decomposed by water.

Sesquisulphuret of Antimony.—This is by far the most abundant ore of antimony, and is hence employed in making the preparations of antimony. Though generally compact or earthy, it sometimes occurs in acicular crystals and in rhombic prisms. Its sp. gravity is 4.62, colour red-gray, and its lustre metallic. When heated in close vessels, it enters into fusion without undergoing any other change. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of hydrosulphuric acid gas through a solution of tartar emetic: in this case it falls as a hydrate of an orange-red colour, and does not acquire its dark colour till its water is expelled by heat.

The *bisulphuret* is formed, according to Rose, by transmitting hydrosulphuric acid gas through a solution of antimonious acid in dilute hydrochloric acid. (An. of Phil. N. S. x.)

Rose formed the *persulphuret* by the action of hydrosulphuric acid on a solution of antimonic acid. The golden sulphuret, prepared by boiling sulphuret of antimony and sulphur in solution of potassa, a process which is not adopted by either of our colleges, is a persulphuret.

Oxy-sulphuret of Antimony.—Rose has shown that this compound occurs in the mineral kingdom, being the *red antimony ore* (rothspiesglanzerz) of mineralogists. The pharmaceutic preparations known by the terms *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition. They are made by roasting the native sulphuret, so as to form sulphurous acid and sesquioxide of antimony, and then vitrefying the oxide together with undecomposed ore, by means of a strong heat. The product will of course differ according as more or less of the sulphuret escapes oxidation during the process.

When sulphuret of antimony is boiled in a solution of potassa or soda, a liquid is obtained, from which on cooling an orange-red matter called *kermes mineral* is deposited; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *golden sulphuret* of the Pharmacopœia, subsides. These compounds may also be obtained by igniting sulphuret of antimony with an alkali or alkaline carbonate, and treating the product with hot water; or by boiling the mineral in a solution of carbonate of soda or potassa. The finest kermes is obtained, according to M. Cluzel, from a mixture of 4 parts of sulphuret of antimony, 90 of crystallized carbonate of soda, and 1000 of water. These materials are boiled for half or three-quarters of an hour; the hot solution is filtered into a warm vessel, in order that it may cool slowly; and after 24 hours, the deposite is collected on a filter, moderately washed with cold water, and dried at a temperature of 70° or 80° F.

Very great diversity of opinion has long existed among chemists as to the nature of kermes. Berzelius and Rose gave experiments to show that it is a hydrated sesquisulphuret, differing from the native sulphuret solely in being combined with water. Subsequently Gay-Lussac and others observed that kermes contains sesquioxide of antimony, which may be removed by digestion with cream of tartar; and Gay-Lussac inferred from the quantity of water formed when kermes, previously rendered anhydrous, is reduced by hydrogen gas, that it is a hydrated oxy-sulphuret, identical, when deprived of its water, with the red ore of antimony above referred to. Still more recently Berzelius has explained, that the ordinary process for making kermes leads to the separation of a compound of sesquioxide of antimony and potassa, which tenaciously adheres to kermes, but is not chemically united with it: he rightly argues that the question is not, whether sesquioxide of antimony is sometimes or generally present in kermes, but whether the latter can exist *without* sesquioxide of antimony. This question he has answered affirmatively. He fused sulphuret of antimony with black flux, boiled the residue in water, and set aside the solution to cool: a perfect kermes was deposited, which he considers, and I apprehend with good reason, to be quite free from sesquioxide of antimony. (Pog. Annalen, xx. 364.)

The theory of the preparation of kermes, as given by Berzelius, is the following.—When sesquisulphuret of antimony is fused with potassa, part of each interchanges elements with the other in such a ratio that

1 eq. sesquisulphuret of ant. $2Sb+3S$ yield 1 eq. sesquioxide of antimony $2Sb+3O$
and 3 eq. potassa $3(K+O)$ & 3 eq. sulphuret of potassium $3(K+S)$.

The sulphuret of potassium unites with undecomposed sesquisulphuret of antimony, forming a sulphur-salt which will be again referred to hereafter, and sesquioxide of antimony with undecomposed potassa; and on adding hot water both compounds are dissolved, and coexist independently of each other in the solution. As the solution cools, the sesquisulphuret of antimony subsides, simply because the solvent power of sulphuret of potassium is thereby diminished; but a variable quantity of potassa and sesquioxide of antimony falls with the deposite, and cannot be entirely removed by washing with water. The cold solution still contains a double sulphuret of antimony and potassium, together with sesquioxide of antimony united with potassa: on acidulating with sulphuric acid, the sulphuret of potassium is resolved, by decomposition of water, into potassa and hydrosulphuric acid, and the sesquioxide of antimony is deprived of its potassa; and, therefore, the sesquisulphuret and sesquioxide of antimony, both losing at the same instant the principles which gave them solubility, are thrown down either in combination or in mixture with each other. Berzelius believes the same change to occur when the ingredients are boiled instead of fused together. The golden sulphuret differs from kermes, in the absence of potassa, in containing more sesquioxide of antimony, and perhaps in being or containing an oxy-sulphuret. It commonly contains free sulphur, derived apparently from the oxidizing influence of the air on the sulphuret of potassium. When alkaline carbonates are employed instead of pure alkalies, the same phenomena ensue, except that carbonic acid is evolved.

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SECTION XX.

URANIUM—CERIUM.

URANIUM.

This metal was discovered in 1789 by the German analyst Klaproth, who named it after the new planet Uranus, the discovery of which took place in the same year. It was obtained from a mineral of Saxony, called from its black colour *pitchblende*, which consists of protoxide of uranium and oxide of iron. From this ore the uranium may be conveniently extracted by the following process.—After heating the mineral to redness, and reducing it to fine powder, it is digested in pure nitric acid diluted with three or four parts of water, taking the precaution to employ a larger quantity of the mineral than the nitric acid present can dissolve. By this mode of operating, the protoxide is converted into peroxide of uranium, which unites with the nitric acid almost to the total exclusion of the iron. A current of hydrosulphuric acid gas is then transmitted through the solution, in order to separate lead and copper, the sulphurets of which are always mixed with pitchblende. The solution is boiled to expel free hydrosulphuric acid, and, after being concentrated by evaporation, is set aside to crystallize. The nitrate of peroxide of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

The properties of metallic uranium are as yet known imperfectly. It was prepared by Arfwedson by conducting hydrogen gas over the protoxide of uranium heated in a glass tube. The substance obtained by this process was crystalline, of a metallic lustre, and of a reddish-brown colour. It suffered no change on exposure to air at common temperatures; but when heated in open vessels it absorbed oxygen, and was reconverted into the protoxide. From its lustre it was inferred to be metallic uranium.

From the experiments of Arfwedson and Berzelius on the oxides of uranium, the equivalent of the metal may be estimated at 217. (An. of Ph. N. S. vii. 258.) Its compounds described in this section are thus constituted:

	Uranium.			Equiv.	Formulæ.
Protoxide	217	1 eq. + Oxygen	8	1 eq. = 225	$U + O$ or $\dot{U}$.
Peroxide	434	2 eq. + do.	24	3 eq. = 458	$2U + 3O$ or $\underline{\dddot{U}}$.
Protochloride	217	1 eq. + Chlorine	35.42	1 eq. = 252.42	$U + Cl$ or UCl.
Perchloride	434	2 eq. + do.	106.26	3 eq. = 540.26	$2U + 3Cl$ or U^2Cl^3.
Sulphuret.	Composition unknown.				

Protoxide.—This oxide is of a very dark green colour, and is obtained by exposing nitrate of the peroxide to a strong heat. It is exceedingly infusible, and bears any temperature hitherto tried without change. It unites with acids, forming salts of a green colour. It is readily oxidized by nitric acid, yielding a nitrate of the peroxide. The protoxide is employed in the arts for giving a black colour to porcelain.

Peroxide of Uranium is of a yellow or orange colour, and most of its salts have a similar tint. It not only combines with acids, but likewise unites with alkaline bases, a property which was first noticed by Arfwedson. It is precipitated from acids as a yellow hydrate by pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by alkaline carbonates, but is redissolved by an excess of carbonate of soda or ammonia, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by hydrosulphuric acid, but acquires a green tint from partial deoxidation. With ferrocyanuret of potassium it gives a brownish-red precipitate, very like ferrocyanuret of copper.

Peroxide of uranium is decomposed by a strong heat, and converted into the protoxide. From its affinity for alkalies, it is difficult to obtain it in a state of perfect purity. It is employed in the arts for giving an orange colour to porcelain.

Chlorides.—These compounds are obtained in solution by dissolving the corresponding oxides in hydrochloric acid. The *protochloride* is green, very soluble, and does not crystallize. The *perchloride* is yellow, deliquescent, soluble in alcohol, ether, and water, and yields yellow solutions.

Sulphuret of Uranium may be formed by transmitting the vapour of bisulphuret of carbon over protoxide of uranium strongly heated in a tube of porcelain. (Rose.) It is of a dark gray or nearly black colour, is converted into protoxide of uranium when heated in the open air, and is readily dissolved by nitric acid. Hydrochloric acid attacks it feebly.

CERIUM.

Cerium, named after the planet Ceres, was discovered in the year 1803 by Hisinger and Berzelius, in a rare Swedish mineral known by the name of cerite, and its existence was recognized about the same time by Klaproth. Dr. Thomson has since found it to the extent of thirty-four per cent. in a mineral from Greenland, called *Allanite*, in honour of the late Mr. Allan, who first distinguished it as a distinct species.

The properties of cerium are in a great measure unknown. It appears from the experience of Vauquelin, who obtained it in minute buttons not larger than the head of a pin, that it is a white brittle metal, which resists the action of nitric, but is dissolved by nitro-hydrochloric acid. According to an experiment made by Mr. Children and Dr. Thomson, metallic cerium is volatile in very intense degrees of heat. (An. of Phil. ii.)

From the experiments of Hisinger, the equivalent of cerium may be estimated at 46, and its compounds described in this section are thus constituted:—

	Cerium.			Equiv.	Formulæ.
Protoxide	46	1 eq.+Oxygen	8	1 eq.= 54	$Ce+O$ or $\dot{Ce}$.
Peroxide	92	2 eq.+do.	24	3 eq.=116	$2Ce+3O$ or $\underline{\dddot{Ce}}$.
Protochloride	46	1 eq.+Chlorine	35.42	1 eq.= 81.42	$Ce+Cl$ or $CeCl$.
Perchloride	92	2 eq.+do.	106.26	3 eq.=198.26	$2Ce+3Cl$ or Ce^2Cl^3.
Protosulphuret	46	1 eq.+Sulphur	16.1	1 eq.= 62.1	$Ce+S$ or CeS.

Protoxide.—This oxide is a white powder, which is insoluble in water, and forms salts with acids, all of which if soluble have an acid reaction. Exposed to the air at common temperatures it suffers no change; but if heated in open vessels, it absorbs oxygen, and is converted into the peroxide. It is precipitated from its salts as a white hydrate by pure alkalies; as a white carbonate by alkaline carbonates, but is redissolved by the precipitant in excess; and as a white oxalate by oxalate of ammonia.

Peroxide of Cerium has a fawn-red colour. It is dissolved by several of the acids, but is a weaker base than the protoxide. Digested in hydrochloric acid, chlorine is disengaged and a protochloride results.

The most convenient method of extracting peroxide of cerium from cerite is by the process of Laugier. After reducing cerite to powder, it is dissolved in nitro-hydrochloric acid, and the solution is evaporated to perfect dryness. The soluble parts are then redissolved by water, and an excess of ammonia is added. The precipitate thus formed, consisting of the oxides of iron and cerium, is well washed and afterwards digested in a solution of oxalic acid, which dissolves the iron, and forms an insoluble oxalate with the cerium. By heating this oxalate to redness in an open fire, the acid is decomposed, and the peroxide of cerium is obtained in a pure state.

Chlorides of Cerium.—The *protochloride* is obtained as a porous white mass by heating protosulphuret of cerium in a current of dry chlorine gas. It is fusible at a low red heat, deliquesces in the air, and is soluble in water and alcohol. Its solution is colourless; but in open vessels it becomes yellow from the formation of perchloride, undergoing the same kind of change as the protochlorides of iron and tin.

The *perchloride* is formed by dissolving peroxide of cerium in hydrochloric acid, and it forms an orange-yellow solution.

Protosulphuret of Cerium.—Dr. Mosander has succeeded in forming this compound by two different processes. The first method is by transmitting the vapour of sulphuret of carbon over carbonate of protoxide of cerium at a red heat; and the second is by fusing oxide of cerium at a white heat with a large excess of persulphuret of potassium and afterwards removing the soluble parts by water. The product of the first operation is porous, light, and of a red colour like red lead; and that of the second is in small brilliant scales, and of a yellow colour, like bisulphuret of tin. These sulphurets, though different in appearance, are similar in point of composition, containing 26 per cent. of sulphur. They are insoluble in water, but are dissolved in acids with evolution of hydrosulphuric acid gas, without any residuum of sulphur. (Philos. Mag. and Annals, i. 71).

SECTION XXI.

BISMUTH.—TITANIUM.—TELLURIUM.

BISMUTH.

This metal was known to the ancients, though often confounded by them with lead and tin; but it appears to have derived the name of *bismuth*, or properly *wismuth*, from the German miners. It occurs in the earth both native and in combination with other substances, such as sulphur, oxygen, and arsenic. That which is employed in the arts is derived chiefly from native bismuth, and commonly contains small quantities of sulphur, iron, and copper. It may be obtained pure for chemical purposes by heating the oxide or subnitrate to redness along with charcoal.

Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled, it crystallizes in octohedrons. Its density is about 9.8. It is brittle when cold, but may be hammered into plates while warm. At 476° it fuses, and sublimes in close vessels at a red heat. It is a less perfect conductor of heat than most other metals.

Bismuth undergoes little change by exposure to air at common temperatures. When fused in open vessels, its surface becomes covered with a gray film, which is a mixture of metallic bismuth with the oxide of the metal. Heated to its subliming point it burns with a bluish-white flame, and emits copious fumes of oxide of bismuth. The metal is attacked with difficulty by hydrochloric or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

The equivalent of bismuth, deduced by Lagerhjelm from the composition of its protoxide, is 71. (An. of Phil. iv. 357.) Its compounds described in this section are thus constituted:—

	Bismuth.				Equiv.	Formulæ.
Protoxide	71	1 eq. +	Oxygen	8	1 eq. = 79	$\mathrm{Bi} + \mathrm{O}$ or $\dot{\mathrm{Bi}}$.
Peroxide	142	2 eq. +	do.	24	3 eq. = 166	$2\mathrm{Bi} + 3\mathrm{O}$ or $\dddot{\mathrm{Bi}}$.
Chloride	71	1 eq. +	Chlorine	35.42	1 eq. = 106.42	$\mathrm{Bi} + \mathrm{Cl}$ or $\mathrm{Bi}\overline{\mathrm{Cl}}$.
Bromide	71	1 eq. +	Bromine	78.4	1 eq. = 149.4	$\mathrm{Bi} + \mathrm{Br}$ or BiBr.
Sulphuret	71	1 eq. +	Sulphur	16.1	1 eq. = 87.1	$\mathrm{Bi} + \mathrm{S}$ or BiS.

Protoxide of Bismuth.—This compound is readily prepared by heating to redness the nitrate or subnitrate of oxide of bismuth. Its colour is yellow; at a full red heat it is fused into a brown liquid, which on cooling becomes a yellow transparent glass of sp. gravity 8.211. At intense temperatures it is sublimed. It unites with acids, and most of its salts are white.

When nitrate of oxide of bismuth, either in solution or in crystals, is put into water, a copious precipitate, the subnitrate, of a beautifully white colour, subsides, which was formerly called the *magistery of bismuth.* From its whiteness it is sometimes employed as a paint for improving the complexion; but it is an inconvenient pigment, owing to the facility with which it is blackened by hydrosulphuric acid. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, nearly the whole of the bismuth is separated as a subnitrate.—By this character bismuth may be both distinguished and separated from other metals.

Peroxide.—This oxide was first noticed by Buchholz and Brandes, but its nature and composition have been recently examined by Mr. A. Stromeyer. It is generated when hydrate of potassa is fused at a moderate heat with protoxide of bismuth; but the best mode of preparation is first to prepare the protoxide by igniting the subnitrate, and then gently heating it for some time in a solution of chloride of potassa or soda. After washing with water, any unchanged protoxide is dissolved by a solution made with 1 part of nitric acid (quite free from nitrous acid) and 9 of water.

As thus prepared, peroxide of bismuth is a heavy powder of a brown colour, very like peroxide of lead, manifests little disposition to unite either with acids or alkalies, and is reconverted by heat with loss of oxygen into the protoxide. Heated with sulphuric or phosphoric acid, it gives off oxygen gas, and a sulphate or phosphate of the protoxide is formed; and with hydrochloric acid, chlorine is evolved, and the protochloride produced. (An. de Ch. et de Ph. li. 267.)

Chloride of Bismuth.—When bismuth in fine powder is introduced into chlorine gas, it takes fire, burns with a pale blue light, and is converted into a chloride, formerly termed *butter* of bismuth. It may be prepared conveniently by heating two parts of corrosive sublimate with one of bismuth, and afterwards expelling the excess of the former, together with the metallic mercury, by heat.

Chloride of bismuth is of a grayish-white colour, opaque, and of a granular texture. It fuses at a temperature a little above that at which the metal itself is liquefied, and bears a red heat in close vessels without subliming.

Bromide of Bismuth is prepared by heating the metal with a large excess of bromine in a long tube; when a gray-coloured bromide results, similar in its aspect to fused iodine. At 392° it enters into fusion, and at a low red heat sublimes. With water it is converted into oxide of bismuth and hydrobromic acid, the former of which combines with some undecomposed bromide of bismuth as an oxy-bromide. (Serullas.)

Sulphuret of Bismuth.—This sulphuret is found native, and may be formed artificially by fusing bismuth with sulphur, or by the action of hydrosulphuric acid on the salts of bismuth. It is of a lead gray colour, and metallic lustre.

TITANIUM.

This metal was first recognized as a new substance by Mr. Gregor of Cornwall, and its existence was afterwards established by Klaproth, who fancifully gave it the name of *titanium*, after the *Titans* of ancient fable. (Contributions, i.) But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Dr. Wollaston was led to examine some minute crystals which were found in a slag at the bottom of a smelting furnace at the great iron works at Merthyr Tydvil in Wales, and presented to him by the Rev. Dr. Buckland. (Philosophical Transactions, 1823.) These crystals, which have since been found at other iron works, are of a cubic form, and in colour and lustre resemble burnished copper. They conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their sp. gravity is 5.3; and their hardness is so great, that they scratch a polished surface of rock crystal. They are exceedingly infusible; but when exposed to the united action of heat and air, their surface becomes covered with a purple-coloured film, which is an oxide. They resist the action of nitric and nitro-hydrochloric acids, but are completely oxidized by being strongly heated with nitre. They are then converted into a white substance, which possesses all the properties of titanic acid.

Liebig prepares metallic titanium by putting fragments of recently made chloride of titanium and ammonia into a glass tube half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and, when atmospheric air is entirely displaced, applying heat until the glass softens. Complete decomposition ensues, nitrogen gas is disengaged, hydrochlorate of ammonia sublimes, and metallic titanium is left in the state of a deep blue-coloured powder. If exposed to the air while warm, it is apt to take fire.

The equivalent of titanium, determined by Rose from his analysis of the bichloride, is 24.3. The composition of its compounds described in this section is as follows:—

	1 eq. Titanium.		Equiv.	Formulæ.
Oxide (probably)	24.3 + Oxygen	8	1 eq.=32.3	$Ti+O$ or $\dot{Ti}$.
Titanic acid .	24.3 + do	16	2 eq.=40.3	$Ti+2O$ or $\ddot{Ti}$.
Bichloride . .	24.3 + Chlorine	70.84	2 eq.=95.14	$Ti+2Cl$ or $TiCl_2$.
Bisulphuret .	24.3 + Sulphur	32.2	2 eq.=56.5	$Ti+2S$ or TiS^2.

Oxide of Titanium.—This oxide is of a purple colour, and is supposed to exist pure in the mineral called *anatase;* but its composition and chemical properties are unknown.

Titanic Acid.—This compound, called also *peroxide of titanium*, exists in a nearly pure state in titanite or rutile. Menaccanite, in which titanium was originally discovered by Mr. Gregor, is a titanite of the oxides of iron and manganese. It is best prepared from rutile. The mineral, after being reduced to an exceedingly fine powder, is fused in a platinum crucible with three times its weight of carbonate of potassa, and the mass afterwards washed with water to remove the excess of alkali. A gray mass remains, which consists of potassa and titanic acid. This compound is dissolved in concentrated hydrochloric acid; and on diluting with water, and boiling the solution, the greater part of the titanic acid is thrown down. It is then collected on a filter, and well washed with water acidulated with hydrochloric acid. In this state the oxide is not quite pure; but contains a little oxide of manganese and iron, derived from the rutile. The best mode of separating these impurities is to digest the precipitate, while still moist, with hydrosulphate of ammonia, which converts the oxides of iron and manganese into sulphurets, but does not act on the titanic acid. The two sulphurets are readily dissolved by dilute hydrochloric acid; and the titanic acid, after being collected on a filter and well washed as before, may be dried and heated to redness. This method, proposed by Professor Rose of Berlin, has been thus simplified by himself. Either rutile or titaniferous iron, after being pulverized and washed, is exposed in a porcelain tube at a very strong red heat to a current of hydrosulphuric acid gas, which acts upon the oxide of iron, giving rise to water and sulphuret of iron. As soon as water ceases to appear, the process is discontinued, the mass digested in hydrochloric acid to remove the iron, and the titanic acid separated from adhering sulphur by heat. A little iron is still usually retained; but the whole may be removed by a repetition of the same process. (An. de Ch. et de Ph. xxiii. and xxxviii. 131.)

Titanic acid, when pure, is quite white. It is exceedingly infusible and difficult of reduction; and after being once ignited it ceases to be soluble in acids, except in the hydrofluoric. In its chemical relations it is analogous to silicic acid, being a feeble acid, insoluble in water, without action on test paper, but combining with metallic oxides. In the state of hydrate, as when precipitated from hydrochloric acid by boiling, or when combined with an alkali after fusion, it has a singular tendency to pass through the pores of a filter when washed with pure water; but the presence of a little acid, alkali, or a salt, prevents this inconvenience.

If previously ignited with carbonate of potassa, titanic acid is soluble in dilute hydrochloric acid; but it is retained in solution by so feeble an attraction, that it is precipitated merely by boiling. It is likewise thrown down by the pure and carbonated alkalies, both fixed and volatile. A solution of gall-nuts causes an orange-red colour, which is very characteristic of titanic acid, an effect which appears owing to tannin, and not to gallic acid. When a rod of zinc is suspended in the solution, a purple-coloured powder, probably the protoxide, is precipitated, which is gradually converted into titanic acid.

Bichloride of Titanium.—This substance was discovered in the year 1824 by Mr. George of Leeds, by transmitting dry chlorine gas over metallic titanium at a red heat. Rose prepared it for his analysis by heating a mixture of titanic acid and charcoal in a tube, through which dry chlorine gas was passing: the resulting bichloride was purified from adhering free chlorine by agitation either with mercury or potassium, and repeated distillation. At common temperatures it is a transparent colourless fluid of considerable specific gravity, boils violently at a temperature a little above 212°, and condenses again without change. Dumas has shown that the density of its vapour may be estimated at 6.615. In open vessels it is attacked by the moisture of the atmosphere, and emits dense white fumes of a pungent odour similar to that of chlorine, but not so offensive. On adding a few drops of water to a few drops of the liquid, combination ensues with almost explosive violence, from the evolution of intense heat; and if the water is not in excess a solid hydrate is obtained. On exposure to the air it deliquesces, and on adding water the greater part is dissolved. The bichloride, when exposed to an atmosphere of dry ammonia, absorbs a large quantity of the gas, and becomes solid. It was from this compound Liebig prepared metallic titanium.

Bisulphuret of Titanium.—This compound was discovered by Rose, who prepared it by transmitting the vapour of bisulphuret of carbon over titanic acid, heated to whiteness in a tube of porcelain. It occurs in thick green masses, which by the least friction acquire a dark yellow colour and metallic lustre. When heated in the open air, it is converted into sulphurous and titanic acids. By acids it is slowly decomposed, and is dissolved by hydrochloric acid with disengagement of hydrosulphuric acid gas.

TELLURIUM.

Tellurium is a rare metal, hitherto found only in the gold mines of Transylvania, and even there in very small quantity. Its existence was inferred by Muller in the year 1782, and fully established in 1798 by Klaproth, who gave it the name of *tellurium*, from *tellus*, *the earth*, suggested by the source from which he drew the name of uranium. (Contributions, iii.) It occurs in the metallic state, chiefly in combination with gold and silver.

Tellurium has a tin-white colour running into lead-gray, a strong metallic lustre, and lamellated texture. It is very brittle, and its density is 6.115. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blowpipe it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in gray-coloured pungent inodorous fumes. The odour of decayed horse-radish is sometimes emitted during the combustion, and was thought by Klaproth to be peculiar to tellurium; but Berzelius ascribes it solely to the presence of selenium.

From some late experiments of Berzelius the equivalent of tellurium is 64.2, being nearly double the number stated in the table at page 141. Its compounds described in this section are thus constituted:—

	One eq. Tellurium.			Equiv.	Formulæ.
Tellurous acid	64.2 + Oxyg.	16	2 eq. =	80.2	$\text{Te}+2\text{O}$ or $\ddot{\text{Te}}$
Telluric acid	64.2 + do.	24	3 eq. =	88.2	$\text{Te}+3\text{O}$ or $\dddot{\text{Te}}$.
Chloride	64.2 + Chlor.	35.42	1 eq. =	99.62	$\text{Te}+\text{Cl}$ or TeCl.
Bichloride	64.2 + do.	70.84	2 eq. =	135.04	$\text{Te}+2\text{Cl}$ or TeCl^2.
Bisulphuret	64.2 + Sulph.	32.2	2 eq. =	96.4	$\text{Te}+2\text{S}$ or TeS^2.
Persulphuret	Composition uncertain.				
Hydrotelluric acid	64.2 + Hydr.	1	1 eq. =	65.2	$\text{Te}+\text{H}$ or TeH.

Tellurous Acid.—This compound, also called *oxide of tellurium*, is generated by the action of nitric acid on tellurium, by which acid it is dissolved; but the solution possesses such little permanence that mere affusion of water precipitates part of it, and the rest is obtained by evaporating to dryness. In this state, it is a white granular anhydrous powder, which slowly reddens moist litmus paper, and is insoluble in water and acids. By pure potassa or soda in solution it is dissolved, and is rendered soluble by fusion with the alkaline carbonates, forming with those alkalies crystallizable salts. Acids, added in slight excess to the alkaline solutions, throw down tellurous acid as a white flaky hydrate, which if washed in ice-cold water, and dried at a temperature not exceeding 53°, may be preserved unchanged. In this state it is freely soluble in acids, in ammonia, in the alkaline carbonates, from which it expels carbonic acid, and even to considerable extent in pure water. Its aqueous solution reddens litmus paper: it becomes turbid at 68°, and the acid which falls is no longer soluble in acids. In these properties tellurous acid closely resembles the titanic and several other feeble acids, which have a soluble hydrated state easily convertible into an insoluble anhydrous one. Its salts are precipitated black by hydrosulphuric acid, bisulphuret of tellurium being formed. It is deoxidized, when metallic tellurium falls as a black powder, when a piece of zinc, tin, iron, or antimony is left in its solution.

Telluric Acid.—The process which Berzelius recommends for preparing this compound is either to deflagrate tellurous acid with nitre, or to mix pure potassa freely with a solution of tellurite of potassa, and to saturate fully with chlorine. Nitric acid in slight excess and a little chloride of barium are added, in order to precipitate any traces of sulphuric and selenic acids: and after separating the precipitate by filtration, the liquid is exactly neutralized with ammonia, and chloride of barium added as long as it causes a precipitate. The tellurate of baryta is washed, dried by a gentle heat, and then digested with a fourth of its weight of strong sulphuric acid previously diluted with water: the filtered solution is then concentrated by a water bath, and, on cooling or subsequent spontaneous evaporation, yields hydrated telluric acid in the form of flat six-sided prisms. Adhering sulphuric acid is removed by alcohol.

This hydrate consists of one eq. of acid and three eq. of water. When heated at 212° it loses two of its equivalents of water; and on heating still further all its water is expelled, and the anhydrous acid of a lemon-yellow colour remains. In this state it is insoluble in all fluids, whereas the hydrated acid is soluble in water; and the salts of the former differ from those which the latter forms with the same bases. Hence heat modifies the character of telluric acid much in the same way as that of phosphoric acid. At a heat beyond that required to render it anhydrous, telluric acid loses oxygen and is reduced to tellurous acid. (Pog. Annalen, xxviii. 392.)

Chloride.—Rose obtained it by passing a feeble current of chlorine gas over tellurium at a strong heat, when the chloride passes over as a violet vapour, which at first condenses into a black liquid, and when quite cold becomes a solid of the same colour. By the action of water it deposites metallic tellurium, and the bichloride is dissolved.

Bichloride.—Rose obtained this in the same manner as the preceding chloride, except using a lower heat and a more liberal supply of chlorine.

The bichloride is also volatile, and, after being purified from free chlorine by agitation with mercury, and a second distillation, it condenses into a white crystalline solid. By a gentle heat it yields a brown liquid, but recovers its whiteness on cooling. (Pog. Annalen, xxi. 443.)

Bisulphuret.—This compound falls of a dark brown, nearly black colour, when hydrosulphuric acid gas is transmitted through a solution of bichloride of tellurium, tellurous acid, or any soluble tellurite. This sulphuret is what Berzelius calls a sulphur-acid, forming a soluble sulphur-salt by uniting with sulphuret of potassium. Hence a solution of caustic potassa dissolves bisulphuret of tellurium, producing the same kind of change as on sulphuret of antimony. (Page 379.)

Persulphuret.—This compound falls of a deep yellow colour, when a salt of telluric acid is mixed in solution with persulphuret of potassium. Its existence is but transient, as it is quickly transformed into bisulphuret and becomes black.

Hydrotelluric Acid.—This gas, discovered by Davy in 1809, is formed by acting with hydrochloric acid on an alloy of tellurium with zinc or tin. It has the properties of a feeble acid, very analogous in odour, and apparently in composition, to hydrosulphuric acid; it is absorbed by water, forming a claret-coloured solution; and it precipitates many metallic salts, yielding an alloy of tellurium with the other metal. It is deprived of its hydrogen by chlorine, nitric acid, or oxygen of the atmosphere, tellurium being separated.

SECTION XXII.

COPPER.

Copper is one of the most abundant of the metals, and was well known to the ancients. Native copper is by no means uncommon, being found more or less in most copper mines: it occurs in large amorphous masses in some parts of America, and is sometimes met with in octohedral crystals or in some of the forms allied to the octohedron. Stromeyer has lately discovered it in several specimens of meteoric iron, but in a quantity not exceeding 2-1000ths of the mass. The copper of commerce is extracted chiefly from the native sulphuret; especially from copper pyrites, a double sulphuret of iron and copper. The first part of the process consists in roasting the ore, so as to burn off some of the sulphur, and leave the remainder as a subsulphate of the oxides of iron and copper. The mass is next heated with some unroasted ore and siliceous substances, by which means much of the iron unites in the state of black oxide with silicic acid, and rises as a fusible slag to the surface; while most of the copper returns to the state of sulphuret. It is then subjected to long-continued roasting, when the greater part of the sulphur escapes as sulphurous acid and the metal is oxidized; after which it is reduced by charcoal, and more of the iron separated as a silicate by the addition of sand. Lastly, the metal is strongly heated while a current of air plays upon its surface: the impurities, chiefly sulphur and iron, being more oxidable than copper, combine with oxygen by preference, and the copper is at length left in a state of purity sufficient for the purposes of commerce.

Copper is distinguished from all other metals, titanium excepted, by having a red colour. It receives a considerable lustre by polishing. Its density, when fused, is 8.895, and it is increased by hammering. It is both ductile, and malleable, and in tenacity is inferior only to iron. It is hard and elastic, and consequently sonorous. Its point of fusion is 1996° F. according to Mr. Daniell, being less fusible than silver and more so than gold.

Copper undergoes little change in a perfectly dry atmosphere; but is rusted in a short time by exposure to air and moisture, being converted into a green substance, carbonate of the black oxide of copper. At a red heat it absorbs oxygen, and is converted into black scales of oxide. It is attacked with difficulty by hydrochloric and sulphuric acids, and not at all by solutions of the vegetable acids, if atmospheric air be excluded; but if air have free access, the metal absorbs oxygen with rapidity, the attraction of the acid for the oxide of copper co-operating with that of the copper for oxygen. Nitric acid acts with violence on copper, forming a nitrate of the black oxide.

The most trustworthy experiments for determining the equivalent of copper are those of Berzelius on the reduction of the black oxide by means of hydrogen gas at a red heat. According to the best of his analyses, 8 parts of oxygen unite with 31.6 parts of copper to constitute the black oxide; and, therefore, if this oxide be formed of an atom of oxygen united with an atom of copper, the equivalent of this metal will be 31.6. This opinion, which I have adopted, is maintained by Thomson, Berzelius, and many Continental chemists. Others consider it as a binoxide, regarding red oxide of copper as the real protoxide; and these take twice 31.6 or 63.2 as the equivalent of copper. The principal arguments in favour of the former view are these:—1, the red oxide has very much the character of a *suboxide*, a term frequently used to designate an oxide which has little or no tendency to unite with acids, and which contains less than one atom of oxygen to one atom of metal; 2, the product of the equivalent and specific heat of most metals is a constant quantity, and copper coincides with the law, provided the black oxide contain an atom of each element (page 35); 3, the salts of the black oxide are isomorphous with the salts of protoxide of iron, which gives a strong presumption that these oxides possess the same atomic constitution.

The composition of the compounds described in this section is as follows:—

	Copper.				Equiv.	Formulæ.
Red or dioxide	63.2	2 eq.+Oxygen	8	1 eq.=	71.2	$2Cu+O$.
Black or protoxide	31.6	1 eq.+do.	8	1 eq.=	39.6	$Cu+O$.
Superoxide .	31.6	1 eq.+do.	16	2 eq.=	47.6	$Cu+2O$.
Dichloride .	63.2	2 eq.+Chlorine	35.42	1 eq.=	98.62	$2Cu+Cl$.
Chloride .	31.6	1 eq.+do.	35.42	1 eq.=	67.02	$Cu+Cl$.
Diniodide .	63.2	2 eq.+Iodine	126.3	1 eq.=	189.5	$2Cu+I$.
Disulphuret .	63.2	2 eq.+Sulphur	16.1	1 eq.=	79.3	$2Cu+S$.
Sulphuret .	31.6	1 eq.+do.	16.1	1 eq.=	47.7	$Cu+S$.
Triphosphuret .	94.8	3 eq.+Phosph.	15.7	1 eq.=	110.5	$3Cu+P$.
Subsesquiphosph.	94.8	3 eq.+do.	31.4	2 eq.=	126.2	$3Cu+2P$
Cyanuret .	31.6	1 eq.+Cyanogen	26.39	1 eq.=	57.99	$Cu+Cy$.
Disulphocyanuret	63.2	2 eq.+ Cyan. 26.39 Sulph. 32.2	58.59	1 eq.=	121.79	$2Cu+CyS$

Red Oxide.—This compound occurs native in the form of octohedral crystals, and is found of peculiar beauty in the mines of Cornwall. It may be prepared artificially by heating, in a covered crucible, a mixture of 31.6 parts of copper filings with 39.6 of the black oxide; or still better by arranging thin copper plates one above the other, with interposed strata of the black oxide, and exposing them to a red heat carefully protected from the air. Another method is by boiling a solution of acetate of protoxide of copper with sugar, when the suboxide subsides as a red powder; and another is to fuse at a low red heat the dichloride of copper with about an equal weight of carbonate or bicarbonate of soda, subsequently dissolving the sea-salt by water, and drying the red powder.

In this case, by an interchange of elements,

1 eq. dichloride of copper $2Cu+Cl$ yield 1 eq. red oxide . . . $2Cu+O$
and 1 eq. soda . . . . $Na+O$ and 1 eq. chloride of sodium $Na+C$

The red oxide of copper has a density of 6.093, and in colour is very similar to copper. It may be preserved in a dry atmosphere; but at a red heat it absorbs oxygen, and is converted into the protoxide. Dilute acids act on it very slowly; and the resulting solution, as is indicated by its tint, does not arise from the union of the red oxide itself with the acid, but from its being resolved, like other suboxides, into metal and a protoxide. With strong nitric acid it is oxidized, binoxide of nitrogen escapes, and a nitrate of the black oxide is formed. Strong hydrochloric acid forms with it a colourless solution, from which alkalies throw it down as a hydrate of an orange tint. In this state it readily absorbs oxygen from the air. The red oxide of copper is soluble in ammonia, and the solution is quite colourless; but it becomes blue with surprising rapidity by free exposure to air, owing to the formation of the black oxide.

Black Oxide.—This compound, the *copper black* of mineralogists, is sometimes found native, being formed by the spontaneous oxidation of other ores of copper. It may be prepared artificially by calcining metallic copper, by precipitation from the salts of copper by means of pure potassa, and by heating nitrate of copper to redness. It varies in colour from a dark brown to a bluish-black, according to the mode of formation, and its density is 6.401. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter. It is insoluble in water, and does not affect the vegetable blue colours. It combines with nearly all the acids, and most of its salts have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep blue solution, a property by which protoxide of copper is distinguished from all other substances.

The salts of protoxide of copper are distinguished from most substances by their colour, and are easily recognized by reagents. When pure soda or potassa is mixed with a solution of sulphate of the protoxide, a greenish-blue disulphate at first subsides; but as soon as the alkali is added in excess, a blue bulky hydrate of the oxide is formed, which is decomposed by boiling, and consequently becomes black. Pure ammonia also throws down the disulphate when carefully added; but an excess of the alkali instantly redissolves the precipitate, and forms a deep blue solution. Alkaline carbonates cause a bluish-green precipitate, carbonate of the protoxide, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark brown sulphuret by hydrosulphuric acid, and as a reddish-brown ferrocyanuret by ferrocyanuret of potassium. It is thrown down of a yellowish-white colour by albumen, and M. Orfila has proved that this compound is inert, so that albumen is an antidote to poisoning by copper.

Copper is separated in the metallic state by a rod of iron or zinc. The copper thus obtained, after being digested in a dilute solution of hydrochloric acid, is almost chemically pure.

The best mode of detecting copper, when supposed to be present in mixed fluids, is by hydrosulphuric acid. The sulphuret, after being collected, and heated to redness in order to char organic matter, should be placed on a piece of porcelain, and be digested in a few drops of nitric acid. Sulphate of protoxide of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue tint on the addition of ammonia.

Superoxide.—This oxide was prepared by Thenard by the action of peroxide of hydrogen diluted with water on the hydrated black oxide. It suffers spontaneous decomposition under water; but it may be dried *in vacuo* by means of sulphuric acid.

Dichloride.—When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated. The *dichloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust, who called it *white muriate of copper*, procured it by the action of protochloride of tin on chloride of copper; and also by decomposing the chloride by heat, air being excluded. It is slowly deposited in crystalline grains, when the green solution of chloride of copper is kept in a corked bottle in contact with metallic copper.

The dichloride of copper is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. It is insoluble in water, but dissolves in hydrochloric acid, and is precipitated unchanged by water as a white powder. Its colour varies with the mode of preparation, being white, yellow, or dark brown. It is apt to absorb oxygen from the atmosphere, forming a green-coloured compound of oxide and chloride of copper; a change to which the dichloride prepared in the moist way is peculiarly prone.

Chloride.—The chloride of copper is obtained in solution of a green colour by dissolving protoxide of copper in hydrochloric acid, and crystallizes by due concentration in green needles, which are deliquescent and very soluble in alcohol. When heated, they fuse, lose water, and the anhydrous chloride in form of a yellow powder is left; but the heat must not exceed 400°, as beyond that degree the chloride loses half its chlorine, and is converted into the dichloride.

Diniodide of Copper.—This substance is obtained by adding iodide of potassium to a solution made of the sulphates of the protoxides of copper and iron, both in crystals, in the ratio of 1 to 2½, when the protoxide of iron takes the oxygen of the oxide of copper, and the iodine the metallic copper, forming a white precipitate, the diniodide. It may be dried, and will bear a high temperature in close vessels without change; but if heated with the oxides of iron, manganese, or copper, iodine is expelled, and the copper oxidized. (Page 226.)

Iodide of Copper is scarcely known. For on mixing a salt of oxide of copper with iodide of potassium, iodine is set free and the diniodide of copper falls. A small quantity of iodide of copper remains in solution.

Sulphurets of Copper.—The *disulphuret* is a natural production, well known to mineralogists under the name of *copper glance;* and in combination with protosulphuret of iron, it is a constituent of variegated copper ore. It is formed artificially by heating copper filings with a third of their weight of sulphur, the combination being attended with such free disengagement of heat, that the mass becomes vividly luminous.

Sulphuret of Copper is a constituent of copper pyrites, in which it is combined with protosulphuret of iron. It may be formed artificially by the action of hydrosulphuric acid on a salt of copper. When ignited without exposure to the air, it loses half of its sulphur, and is converted into the disulphuret.

Phosphurets of Copper.—Rose states that the *triphosphuret* is generated by the action of phosphuretted hydrogen gas on dichloride of copper; the mutual interchange of elements being such that

$$\left.\begin{array}{ll}\text{3 eq. dichloride of copper} & 3(2Cu+Cl) \\ \text{and 1 eq. phosphuretted hyd.} & 3H+2P\end{array}\right\}\text{yield}\left\{\begin{array}{ll}\text{2 eq. triphosphuret} & 2(Cu+P) \\ \text{and 3 eq. hydrochl. acid} & 3(H+Cl.)\end{array}\right.$$

The *subsesquiphosphuret* is formed by a similar interchange between chloride of copper and phosphuretted hydrogen, so that

$$\left.\begin{array}{ll}\text{3 eq. chloride of copper} & 3(C+uCl) \\ \text{and 1 eq. phosp. hyd.} & 3H+2P\end{array}\right\}\text{yield}\left\{\begin{array}{ll}\text{1 eq. subsesquiphosphuret} & 3Cu+2P \\ \text{and 3 eq. hydrochloric acid} & 3(H+Cl).\end{array}\right.$$

Rose obtained the *protophosphuret* by the action of hydrogen gas on phosphate of protoxide of copper at a red heat. All these phosphurets resemble each other, being pulverulent, of a gray colour, insoluble in hydrochloric acid, are oxidized and dissolved by nitric acid, and burn with a phosphorus flame before the blowpipe. A phosphuret of copper is also obtained by transmitting phosphuretted hydrogen gas through a solution of sulphate of oxide of copper; but the dark precipitate which falls seems to be a variable mixture of different phosphurets, phosphoric acid being generated at the same time. (An. de Ch. et de Ph. li. 47.)

Cyanuret of Copper.—This compound is formed by the action of hydrocyanic acid on hydrated protoxide of copper, or by mixing the sulphate of that oxide in solution with cyanuret of potassium. It falls as a yellow precipitate, insoluble in water, but soluble in hydrochloric or sulphuric acid.

Disulphocyanuret of Copper.—It appears as a white precipitate, insoluble in most acids, when sulphocyanuret of potassium is added to a mixed solution of the sulphates of the protoxides of copper and iron.

◆

SECTION XXIII.

LEAD.

This metal was well known to the ancients. As a native production it is very rare; but in combination with sulphur it occurs in great quantity. All the lead of commerce is extracted from the native sulphuret, the *galena* of mineralogists. This ore, in the state of coarse powder, is heated in a reverberatory furnace; when part of it is oxidized, yielding sulphate of protoxide of lead, sulphuric acid which is evolved, and free oxide of lead. These oxidized portions then react on sulphuret of lead: by the reaction of two equivalents of oxide of lead and one of the sulphuret, three equivalents of metallic lead and one of sulphurous acid result; while one equivalent of the sulphuret and one of sulphate mutually decompose each other, giving rise to two equivalents of sulphurous acid and two of metallic lead. The slag which collects on the surface of the fused lead contains a large quantity of sulphate of protoxide of lead, and is decomposed by the addition of quicklime, the oxide so separated reacting as before on sulphuret of lead. The lead of commerce commonly contains silver, iron, and copper.

Lead has a bluish-gray colour, and when recently cut, a strong metallic lustre; but it soon tarnishes by exposure to the air, acquiring a superficial coating of carbonate of protoxide of lead. (Christison.) Its density is 11.352. It is soft, flexible, and inelastic. It is both malleable and ductile, possessing the former property in particular to a considerable extent. In tenacity, it is inferior to all ductile metals. It fuses at about 612° F., and when slowly cooled forms octohedral crystals. It may be heated to whiteness in close vessels without subliming.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a gray film is formed upon its surface, which is a mixture of metallic lead and protoxide; and when strongly heated it is dissipated in fumes of the protoxide. In distilled water, previously boiled and preserved in close vessels, it undergoes no change; but in open vessels it is oxidized with considerable rapidity, yielding minute, shining, brilliantly white, crystalline scales of carbonate of the protoxide, the oxygen and the carbonic acid being derived from the air. The presence of saline matter in water retards the oxidation of the lead; and some salts, even in very minute quantity, prevent it altogether. The protecting influence, exerted by certain substances, was first noticed by Guyton-Morveau; but it has been minutely investigated by Dr. Christison of Edinburgh, who has discussed the subject in his excellent Treatise on Poisons. He finds that the preservative power of neutral salts is materially connected with the insolubility of the compound which their acid is capable of forming with lead. Thus, phosphates and sulphates, as well as chlorides and iodides, are highly preservative; so small a quantity as 1-30,000th part of phosphate of soda or iodide of potassium in distilled water preventing the corrosion of lead. In a preservative solution the metal gains weight during some weeks, in consequence of its surface gradually acquiring a superficial coating of carbonate, which is slowly decomposed by the saline matter of the solution. The metallic surface being thus covered with an insoluble film, which adheres tenaciously, all further change ceases. Many kinds of spring water, owing to the salts which they contain, do not corrode lead; and hence, though intended for drinking, it may be safely collected in leaden cisterns. Of this, the water of Edinburgh is a remarkable instance.

Lead is not attacked by the hydrochloric or the vegetable acids, though their presence, at least in some instances, accelerates the absorption of oxygen from the atmosphere in the same manner as with copper. Cold sulphuric acid does not act upon it; but when boiled in that liquid, the lead is slowly oxidized at the expense of the acid. The only proper solvent for lead is nitric acid. This reagent oxidizes it rapidly, and forms with its oxide a salt which crystallizes in opaque octohedrons by evaporation.

From late experiments on the composition of the protoxide of lead, and of the nitrate and sulphate of that oxide, I have deduced 103.6 as the equivalent, a number which agrees very closely with the researches of Berzelius on the same subject. (Phil. Trans. 1833, part ii.) The composition of its compounds described in this section is as follows:—

	Lead.			Equiv.	Formulæ.
Dinoxide	207.2	2 eq. + Oxygen	8	1 eq.=215.2	$2Pb+O$.
Protoxide	103.6	1 eq. + do.	8	1 eq.=111.6	$Pb+O$.
Peroxide	103.6	1 eq. + do.	16	2 eq.=119.6	$Pb+2O$.
Red oxide	310.8	3 eq. + do.	32	4 eq. =342.8	$3Pb+4O$
	or protox. 223.2	or 2eq. + perox.	119.6	or 1eq.	$2\dot{Pb}+\ddot{Pb}$.
Chloride	103.6	1 eq. + Chlorine	35.42	1 eq.=139.02	$Pb+Cl$.
Iodide	103.6	1 eq. + Iodine	126.3	1 eq.=229.9	$Pb+I$.
Bromide	103.6	1 eq. + Bromine	78.4	1 eq.=182	$Pb+Br$.
Fluoride	103.6	1 eq. + Fluorine	18.68	1 eq.=122.28	$Pb+F$.
Sulphuret	103.6	1 eq. + Sulphur	16.1	1 eq.=119.7	$Pb+S$.
Phosphuret Carburet	Composition uncertain.				
Cyanuret	103.6	1 eq. + Cyanogen	26.39	1 eq=129.99	$Pb+Cy$.

Dinoxide of Lead.—Dulong observed that on heating dry oxalate of protoxide of lead in a glass tube to low redness, air being excluded, a mixture of carbonic acid and carbonic oxide gases is evolved, and a suboxide remains of a dark gray, nearly black, colour. Boussingault has lately proved that it is a dinoxide. It does not unite with acids, but is resolved by them into a salt of the protoxide with separation of metallic lead. (An. de Ch. et de Ph. liv. 263.)

Protoxide.—This oxide is prepared on a large scale by collecting the gray film which forms on the surface of melted lead, and exposing it to heat and air until it acquires a uniform yellow colour. In this state it is the *massicot* of commerce; and when partially fused by heat, the term *litharge* is applied to it. As thus procured it is always mixed with the red oxide. It may be obtained pure by adding ammonia to a cold solution of nitrate of protoxide of lead until it is faintly alkaline, washing the precipitated subnitrate with cold water, and when dry, heating it to moderate redness for an hour in a platinum crucible. An open fire should be used, and great care taken to prevent combustible matter in any form from contact with the oxide.

Protoxide of lead is red while hot, but has a rich lemon-yellow colour when cold, is insoluble in water, fuses at a bright red heat, and is fixed and unchangeable in the fire. Its density is 9.4214. The fused protoxide has a highly foliated texture, and is very tough, so as to be pulverized with difficulty. By transmitted light it is yellow; but by reflected light it appears green in some parts and yellow in others. Heated with combustible matters, the protoxide parts with oxygen and is reduced. From its insolubility it does not change the vegetable colours under common circumstances; but when rendered soluble by a small quantity of acetic acid, it has a distinct alkaline reaction. It unites with acids, and is the base of all the salts of lead, most of which are of a white colour.

Protoxide of lead is precipitated from its solutions by pure alkalies as a white hydrate, which is redissolved by potassa in excess; as a white carbonate, which is the well-known pigment *white lead*, by alkaline carbonates; as a white sulphate by soluble sulphates; as a dark brown sulphuret by hydrosulphuric acid; and as yellow iodide of lead by hydriodic acid or iodide of potassium.

With regard to the poisonous property of the salts of lead, a remarkable fact has been observed by my colleague Dr. A. T. Thomson, who has proved that of all the ordinary preparations of lead, the carbonate is by far the most virulent poison. Any salt of lead which is easily convertible into the carbonate, as for instance the subacetate, is also poisonous; but he has given large doses of the nitrate of the protoxide and chloride of lead to rabbits without producing perceptible inconvenience. He finds that acetate of protoxide of lead, mixed with vinegar to prevent the formation of any carbonate, may be freely and safely administered in medical practice.

The best method of detecting the presence of lead in wine or other suspected mixed fluids is by means of hydrosulphuric acid. The sulphuret of lead, after being collected on a filter and washed, is to be digested in nitric acid diluted with twice its weight of water, until the dark colour of the sulphuret disappears. The solution of the nitrate should then be brought to perfect dryness on a watch-glass, in order to expel the excess of nitric acid, and the residue be redissolved in a small quantity of cold water. On dropping a particle of iodide of potassium into a portion of this liquid, yellow iodide of lead will instantly appear.

Protoxide of lead unites readily with earthy substances, forming with them a transparent colourless glass. Owing to this property it is much employed for glazing earthenware and porcelain. It enters in large quantity into the composition of flint glass, which it renders more fusible, transparent, and uniform.

Lead is separated from its salts in the metallic state by iron or zinc. The best way of demonstrating this fact is by dissolving 1 part of acetate of protoxide of lead in 24 of water, and suspending a piece of zinc in the solution by means of a thread. The lead is deposited upon the zinc in a peculiar arborescent form, giving rise to the appearance called *arbor Saturni*.

Red Oxide.—This compound, the *minium* of commerce, is employed as a pigment, and in the manufacture of flint glass. It is formed by oxidizing lead by heat and air without allowing it to fuse, and then exposing it in open vessels to a temperature of 600° or 700°, while a current of air plays upon its surface. It slowly absorbs oxygen and is converted into minium.

This oxide does not unite with acids. When heated to redness it gives off pure oxygen gas, and is reconverted into the protoxide. When digested in nitric acid it is resolved into protoxide and peroxide of lead, the former of which unites with the acid, while the latter remains as an insoluble powder. From the facility with which this change is effected even by acetic acid, most chemists consider red lead, not so much as a definite compound of lead and oxygen, but as a salt composed of the protoxide and peroxide as stated at page 392. This oxide has been long considered as a sesquioxide, an error first corrected by Dalton (New System of Chemistry, ii. 41.), whose observation has been confirmed by Dumas and Phillips. (An. de Ch. et de Ph. xlix. 398, and Phil. Mag. N. S. iii. 125.) Dumas shows that the minium is not uniform in composition, but consists of variable mixtures of the protoxide with real red lead. The former may be oxidized by continued exposure to air and heat, and may be dissolved by acetic acid very much diluted with cold water.

Peroxide.—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; by fusing protoxide of lead with chlorate of potassa, at a temperature short of redness, and removing the chloride of potassium by solution in water; and by transmitting a current of chlorine gas through a solution of acetate of the protoxide of lead. In the last the reaction is such, that

$$\underset{\mathrm{Cl.}}{\text{1 eq. chlorine}}\ \&\ \underset{2(\mathrm{Pb}+\mathrm{O})}{\text{2 eq. protox. lead}}\ \text{yield}\ \underset{\mathrm{Pb}+2\mathrm{O}}{\text{1 eq. perox. lead}}\ \&\ \underset{\mathrm{Pb}+\mathrm{Cl.}}{\text{1 eq. chloride lead}}$$

The chloride is removed by washing with warm water.

Peroxide of lead is of a puce colour, is insoluble in water, and is resolved by strong ox-acids, such as the sulphuric and nitric, into a salt of the protoxide and oxygen gas. With hydrochloric acid it yields chlorine gas and chloride of lead. At a red heat it emits oxygen gas and is converted into the protoxide.

Chloride of Lead.—This compound, sometimes called *horn lead*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding hydrochloric acid or a solution of sea-salt to acetate or nitrate of oxide of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with hydrochloric acid, and separates on cooling in small acicular anhydrous crystals of a white colour. It fuses at a temperature below redness, and forms as it cools a semi-transparent mass, which has a density of 5.133. It bears a full red heat in close vessels without subliming; but in open vessels it smokes from spurious evaporation, loses some of its chlorine and absorbs oxygen, yielding an oxy-chloride of a yellow colour.

Iodide of Lead is easily formed by mixing a solution of hydriodic acid in excess with the nitrate of protoxide of lead dissolved in water; and it is of a rich yellow colour. It is dissolved by boiling water, forming a colourless solution, and is deposited on cooling in yellow crystalline scales of a brilliant lustre.

Bromide of Lead.—It falls as a white crystalline powder, of sparing solubility in water, when a soluble salt of lead is mixed with bromide of potassium in solution. Exposed to heat it fuses into a red liquid which becomes yellow when cold.

Fluoride of Lead is formed by mixing hydrofluoric acid with acetate of protoxide of lead, and falls as an uncrystalline white powder of very sparing solubility. It is soluble in nitric and hydrochloric acids, but is decomposed when the solution is evaporated.

Sulphurets of Lead.—It is probable that lead unites with sulphur in several different proportions; but the only one of these compounds well known to chemists is the native sulphuret, *galena*, which occurs in cubic crystals, or in forms allied to the cube. It may be formed artificially by fusing lead with sulphur, or by the action of hydrosulphuric acid on a salt of lead.

Phosphuret of Lead has been little examined. It may be formed by heating phosphate of oxide of lead with charcoal, by mixing a solution of phosphorus in alcohol or ether with the solution of a salt of lead, or by the action of phosphuretted hydrogen on a similar solution.

Carburet of Lead may be obtained by reducing oxide of lead in a state of fine division and intimate admixture with charcoal. It is also generated when salts of lead, which contain a vegetable acid, are decomposed by heat in close vessels. (Berzelius.)

Cyanuret of Lead falls as a heavy white powder when cyanuret of potassium is mixed with a solution of nitrate of oxide of lead, or hydrocyanic acid with the acetate. It is soluble in nitric acid, and to a considerable extent in hot water, yielding colourless solutions. Heated to gentle redness, it gives out nitrogen gas, and pyrophoric carburet of lead remains.

CLASS II.

ORDER III.

METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY A RED HEAT.

SECTION XXIV.

MERCURY OR QUICKSILVER.

This metal was well known to the ancients. The principal mines from which it is obtained are those of Idria in Carniola, and Almaden in Spain, where it is found both in the native state and combined with sulphur as cinnabar, the latter being the most abundant. From this ore the metal is extracted by heating it with lime or iron filings, by which means the mercury is volatilized and the sulphur retained. As prepared on a large scale it is usually mixed in small quantity with other metals, from which it may be purified by cautious distillation.

Mercury is distinguished from all other metals by being fluid at common temperatures. It has a tin-white colour and strong metallic lustre. It becomes solid at a temperature which is 39 or 40 degrees below zero; and in congealing, it evinces a strong tendency to crystallize in octohedrons. It contracts greatly at the moment of congelation; for while its density at 47° is 13.568, that of frozen mercury is 15.612. When solid it is malleable, and may be cut with a knife. At 662° or near that degree, it enters into ebullition, and condenses again on cool surfaces into metallic globules.

Mercury, if quite pure, is not tarnished in the cold by exposure to air and moisture; but if it contain other metals, the amalgam of those metals oxidizes readily, and collects a film upon its surface. Mercury is said to be oxidized by long agitation in a bottle half full of air, and the oxide so formed was calld by Boerhaave *ethiops per se;* but is very probable that the oxidation of mercury observed under these circumstances was solely owing to the presence of other metals. When mercury is exposed to air or oxygen gas, while in the form of vapour, it slowly absorbs oxygen, and is converted into peroxide of mercury.

The only acids that act on mercury are the sulphuric and nitric acids. The former has no action whatever in the cold; but on the application of heat, the mercury is oxidized at the expense of the acid, pure sulphurous acid gas is disengaged, and a sulphate of mercury is generated. Nitric acid acts energetically upon mercury both with and without the aid of heat, oxidizing and dissolving it with evolution of binoxide of nitrogen.

From some late analyses of the peroxide and chlorides of mercury, I have inferred that its equivalent is 202. (Phil. Trans. 1833, part ii.) The composition of its compounds described in this section is as follows:—

	Mercury.			Equiv.	Formulæ.
Protoxide	202 1 eq. + Oxygen	8	1 eq.	= 210	$Hg + O$ or $\dot{Hg}$.
Peroxide	202 1 eq. + do	16	2 eq.	= 218	$Hg + 2O$ or $\ddot{Hg}$.
Protochloride	202 1 eq + Chlorine	35.42	1 eq.	= 237.42	$Hg + Cl$ or $HgCl$.
Bichloride	202 1 eq. + do	70.84	2 eq.	= 272.84	$Hg + 2Cl$ or $HgCl^2$.
Protiodide	202 1 eq. + Iodine	126.3	1 eq.	= 328.3	$Hg + I$ or HgI.
Sesquiodide	404 2 eq. + do.	378.9	3 eq.	= 782.9	$2Hg + 3I$ or Hg^2I^3.
Biniodide	202 1 eq. + do.	252.6	2 eq.	= 454.6	$Hg + 2I$ or HgI^2.
Protobromide	202 1 eq. + Bromine	78.4	1 eq.	= 280.4	$Hg + Br$ or $HgBr$.

	Mercury.			Equiv.	Formulæ.
Bibromide	202 1 eq.	+ Bromine	156.8 2 eq.	= 358.8	$Hg + 2Br$ or $HgBr^2$.
Protosulphuret	202 1 eq.	+ Sulphur	16.1 1 eq.	= 218.1	$Hg + S$ or HgS.
Bisulphuret	202 1 eq.	+ do.	32.2 2 eq.	= 234.2	$Hg + 2S$ or HgS^2.
Bicyanuret	202 1 eq.	+ Cyano.	52.78 2 eq.	= 228.39	$Hg + 2Cy$ or $HgCy$.

Protoxide.—This oxide, which is a black powder, insoluble in water, is best prepared by the process recommended by Donovan. (An. of Phil. xiv.) This consists in mixing calomel briskly in a mortar with pure potassa in excess, so as to effect its decomposition as rapidly as possible: the protoxide is then washed with cold water, and dried spontaneously in a dark place. These precautions are rendered necessary by the tendency of the protoxide to resolve itself into the peroxide and metallic mercury, a change which is easily effected by heat, by the direct solar rays, and even by daylight. It is on this account very difficult to procure protoxide of mercury in a state of absolute purity.

This oxide is precipitated from its salts, of which the nitrate is the most interesting, as the black protoxide by pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by hydrochloric acid or any soluble chloride; and as the black protosulphuret by hydrosulphuric acid. Of these tests, the action of hydrochloric acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protochloride of tin.

Peroxide.—This oxide may be formed either by the combined agency of heat and air, as already mentioned, or by dissolving mercury in nitric acid, and exposing the nitrate so formed to a temperature just sufficient for expelling the whole of the nitric acid. It is commonly known by the name of *red precipitate.* The peroxide prepared from the nitrate almost always contains a trace of nitric acid, which may be detected by heating it in a clean glass tube by means of a spirit-lamp: a yellow ring, formed of subnitrate of oxide of mercury, collects within the tube just above the part which is heated. (Dr. Clarke.)

Peroxide of mercury, thus prepared, is commonly in the form of shining crystalline scales of a nearly black colour while hot, but red when cold: when very finely levigated, the peroxide has an orange colour. It is soluble to a small extent in water, forming a solution which has an acrid metallic taste, and communicates a green colour to the blue infusion of violets. When heated to redness, it is converted into metallic mercury and oxygen. Long exposure to light has a similar effect. (Guibourt.)

Some of the neutral salts of this oxide, such as the nitrate and sulphate, are converted by water, especially at a boiling temperature, into insoluble yellow subsalts, leaving a strongly acid solution, in which a little of the original salt is dissolved. The oxide is separated from all acids as a red, or when hydratic as a yellow precipitate, by the pure and carbonated fixed alkalies. Ammonia and its carbonate cause a white precipitate, which is a double salt, consisting of one equivalent of the acid, one equivalent of the peroxide, and one equivalent of ammonia. The oxide is readily reduced to the metallic state by metallic copper. Hydrosulphuric acid, phosphorous acid, and protochloride of tin, reduce the peroxide into the protoxide; and when added in larger quantity, the first throws down a black sulphuret, and the two latter metallic mercury. The action of hydrosulphuric acid on a solution of corrosive sublimate is, however, peculiar; for at first it occasions a white precipitate which, according to Rose, is a compound of two equivalents of bisulphuret to one of bichloride of mercury. This gas acts on bibromide and biniodide of mercury in a similar manner. (An. de Ch. et de Ph. xl. 46.)

Protochloride.—Protochloride of mercury, or *calomel*, is always generated when chlorine comes in contact with mercury at common temperatures; and also by the contact of metallic mercury and the bichloride. It may be made by precipitation, by mixing nitrate of protoxide of mercury in solution with hydrochloric acid or any soluble chloride. It is more commonly prepared by sublimation. This is conveniently done by mixing 272.84 parts or one equivalent of the bichloride with 202 parts or one equivalent of mercury, until the metallic globules entirely disappear, and then subliming. When first prepared it is always mixed with some corrosive sublimate, and, therefore, should be reduced to powder and well washed, before being employed for chemical or medical purposes.

Protochloride of mercury is a rare mineral production, called *horn quicksilver*, which occurs crystallized in quadrangular prisms, terminated by pyramids. When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its density is 7.2. At a heat short of redness, but higher than the subliming point of the bichloride, it rises in vapour without previous fusion; but during the sublimation a portion is always resolved into mercury and the bichloride. It is yellow while warm, but recovers its whiteness on cooling. It is distinguished from the bichloride by not being poisonous, by having no taste, and by being exceedingly insoluble in water. Acids have little effect upon it; but pure alkalies decompose it, separating the black protoxide of mercury. When calomel is boiled in a solution of hydrochlorate of ammonia, it is converted into corrosive sublimate and metallic mercury. Chloride of sodium has a similar effect, though in a less degree.

Bichloride.—When mercury is heated in chlorine gas, it takes fire, and burns with a pale red flame, forming the well-known medicinal preparation and virulent poison *corrosive sublimate*, or bichloride of mercury. It is prepared for medical purposes by subliming a mixture of bisulphate of the peroxide of mercury with chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 298.2 parts or one equivalent of the bisulphate, to 117.44 parts or two equivalents of the chloride. Thus,

Bisulphate of Mercury		1 eq.	Chloride of Sodium		2 eq.
Sulphuric acid	80.2 or 2 eq.	$2\overset{\cdots}{S}$.	Chlorine .	70.84 or 2 eq.	2Cl.
Peroxide of mer.	218 or 1 eq.	$\ddot{Hg}$.	Sodium . .	46.6 or 2 eq.	2Na.
	298.2	$\ddot{Hg}+2\overset{\cdots}{S}$.		117.44	2(Na+Cl).

And by mutual interchange of elements they produce

Bichloride of Mercury		1 eq.	Sulphate of Soda		2 eq.
Mercury .	202 or 1 eq.	Hg.	Soda . . .	62.6 or 2 eq. .	$2\dot{Na}$.
Chlorine .	70.84 or 2 eq.	2Cl.	Sulphuric ac.	80.2 or 2 eq. .	$2\overset{\cdots}{S}$.
	272.84	Hg+2Cl.		142.8	$2(\dot{Na}+\overset{\cdots}{S})$.

The products have exactly the same weight (272.84+142.8=415.64) as the compounds (298.2+117.44=415.64) from which they were prepared.

Bichloride of mercury, when obtained by sublimation, is a semi-transparent colourless substance, of a crystalline texture. It has an acrid, burning taste, and leaves a nauseous metallic flavour on the tongue. Its specific gravity is 5.2. When exposed to a heat short of incandescence, it is fused, enters into ebullition from the rapid formation of vapour, and is deposited without further change on cool surfaces as a white crystalline sublimate. It requires twenty times its weight of cold, and only twice its weight of boiling water for solution, and is deposited from the latter, as it cools, in the form of prismatic crystals. Strong alcohol and ether dissolve it in the same proportion as boiling water; and it is soluble in half its weight of concentrated hydrochloric acid at the temperature of 70°. With the chlorides of potassium and sodium, hydrochlorate of ammonia, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself. When its solution in water is agitated with ether, the latter abstracts the bichloride, and rises with it to the surface of the former, thus affording strong evidence of the bichloride having existed as such in the water. Its aqueous solution is gradually decomposed by light, calomel being deposited.

The presence of mercury in a fluid, supposed to contain corrosive sublimate, may be detected by concentrating and digesting it with an excess of pure potassa. Oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit-lamp, and obtained in the form of metallic globules. But in cases of poisoning, when the bichloride is mixed with organic substances, Dr. Christison recommends that the liquid, without previous filtration, be agitated with a fourth of its volume of ether, which separates the poison from the aqueous part, and rises to the surface. The ethereal solution is then evaporated on a watch-glass, the residue dissolved in water, and the mercury precipitated in the metallic state by protochloride of tin at a boiling temperature. If, as is probable, most of the poison is already converted into calomel, and thereby rendered insoluble, as many vegetable fibres should be picked out as possible, and the whole at once digested with protochloride of tin. The organic substances are then dissolved in a hot solution of caustic potassa, and the insoluble parts washed and sublimed to separate the mercury. (Christison on Poisons.)

A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished gold, and to touch the moistened surface with a piece of iron wire or the point of a penknife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. This process was originally suggested by Mr. Sylvester, and has since been simplified by Dr. Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert bichloride of mercury into calomel, a portion of hydrochloric acid being set free at the same time. Some substances effect this change slowly; while others, and especially albumen, produce it in an instant. Thus, when a solution of corrosive sublimate is mixed with albumen, a white flocculent precipitate subsides, which Orfila has shown to be a compound of calomel and albumen, and which he has proved experimentally to be inert. (Toxicologie, vol. i.) Consequently, a solution of the white of eggs is an antidote to poisoning by corrosive sublimate. The muscular and membranous parts, even of a living animal, produce a similar effect; and the causticity of corrosive sublimate seems owing to the destruction of the animal fibre by which the decomposition of the bichloride is accompanied, and which constitutes an essential part of the chemical change.

Protiodide of Mercury.—This compound is obtained by mixing nitrate of protoxide of mercury in solution with iodide of potassium. It is a green powder, insoluble in water, and disposed to resolve itself under the influence of heat or solar light into mercury and the biniodide. However, when the heat is quickly supplied, it is fused and sublimed without material change.

Sesquiodide.—This compound falls as a yellow powder when iodide of potassium is added in solution to the mixed nitrates of the protoxide and peroxide of mercury, the latter being in excess. The precipitate is digested with a solution of sea-salt which takes up any biniodide which may have fallen.

Biniodide.—This compound is formed by mixing nitrate of the peroxide or bichloride of mercury with iodide of potassium in solution, and falls as a rich red-coloured powder of a tint which vies in beauty with that of vermilion, though, unfortunately, the colour is less permanent. Though insoluble in water, it dissolves freely in an excess of either of its precipitants. If taken up in a hot solution of nitrate of peroxide of mercury, the biniodide crystallizes out on cooling in scales of a beautiful red tint. The same crystals separate from a solution in iodide of potassium; but if the liquid be concentrated, a double iodide of mercury and potassium subsides.

The biniodide, when exposed to a moderate heat, gradually becomes yellow; and the particles, though previously in powder, acquire a crystalline appearance. At about 400° it forms a yellow liquid which slowly sublimes in small transparent scales, or in large rhombic tables, when a considerable quantity is sublimed. The crystals retain their yellow colour at 60° if kept very tranquil; but if the temperature be below a certain point, or they are rubbed or touched, they quickly become red. This phenomenon is entirely due to a change in molecular arrangement: the different colours so often witnessed in the same substances at different temperatures, as in peroxide of mercury and the protoxides of lead and zinc, appear to be phenomena of the same nature.

Protobromide of Mercury.—It is precipitated as a white insoluble powder by mixing nitrate of protoxide of mercury with bromide of potassium.

The *bibromide* is a white crystallizable compound, soluble in water and alcohol, fusible and volatile, and in many respects analogous to the bichloride. It is formed by acting on peroxide of mercury with hydrobromic acid, or digesting the preceding compound with bromine.

Sulphurets of Mercury.—The *protosulphuret* may be prepared by transmitting a current of hydrosulphuric acid gas through a dilute solution of nitrate of protoxide of mercury, or through water in which calomel is suspended. It is a black-coloured substance, which is oxidized by digestion in strong nitric acid. When exposed to heat it is resolved into the bisulphuret and metallic mercury.

The *bisulphuret* is formed by fusing sulphur with about six times its weight of mercury, and subliming in close vessels. When procured by this process it has a red colour, and is known by the name of *factitious cinnabar*. Its tint is greatly improved by being reduced to powder, in which state it forms the beautiful pigment *vermilion*. It may be obtained in the moist way by pouring a solution of corrosive sublimate into an excess of hydrosulphate of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when sublimed. The black precipitate formed by the action of hydrosulphuric acid on bicyanuret of mercury, is likewise a bisulphuret. Cinnabar, as already mentioned, occurs native.

When equal parts of sulphur and mercury are triturated together until metallic globules cease to be visible, the dark coloured mass called *ethiops mineral* results, which Mr. Brande has proved to be a mixture of sulphur and bisulphuret of mercury. (Journal of Science, vol. xviii. p. 294.)

Cinnabar is not attacked by alkalies, or any simple acid; but it is dissolved by the nitro-hydrochloric, with formation of sulphuric acid and peroxide of mercury.

Bicyanuret of Mercury.—This compound is best prepared by boiling, in any convenient quantity of water, finely levigated Prussian blue, quite pure and well dried on a sand-bath, with an equal weight of peroxide of mercury in powder, until the blue colour of the pigment entirely disappears. A colourless solution is formed, which, when filtered and concentrated by evaporation, yields crystals of bicyanuret of mercury in the form of quadrangular prisms. The essential part of this process consists in the peroxide of mercury and the Prussian blue exchanging elements, whereby bicyanuret of mercury and peroxide of iron result; but the entire change is very complex and not well understood. Much cyanogen remains behind in the insoluble part; for on digesting it in hydrochloric acid, so as to remove the peroxide of iron, a considerable quantity of Prussian blue is left. This process is so very uneconomical, that I suspect it would be better, as Winckler proposes, to prepare hydrocyanic acid from ferrocyanuret of potassium and sulphuric acid (page 269), and to agitate with peroxide of mercury until the odour of hydrocyanic acid ceases.

Bicyanuret of mercury is colourless and inodorous, has a disagreeable metallic taste, and is highly poisonous. It dissolves very freely in hot water, and crystallizes readily as it cools. By alcohol it is very sparingly dissolved. When heated it is resolved into mercury and cyanogen. (Page 265.)

SECTION XXV.

SILVER.

This metal was known to the ancients. It frequently occurs native in silver mines, both massive and in octohedral or cubic crystals. It is also found in combination with gold, tellurium, antimony, copper, arsenic, and sulphur. In the state of sulphuret it so frequently accompanies galena, that the lead of commerce is rarely quite free from traces of silver.

Silver is extracted from its ores by two processes which are essentially distinct; one of them being contrived to separate it from lead, the other, the process by *amalgamation*, being especially adapted to those ores which are free from lead. The principle of its separation from lead is founded on the different oxidability of lead and silver, and on the ready fusibility of litharge. The lead obtained from those kinds of galena which are rich in sulphuret of silver is kept at a red heat in a flat furnace, with a draught of air constantly playing on its surface: the lead is thus rapidly oxidized; and as the oxide, at the moment of its formation, is fused, and runs off through an aperture in the side of the furnace, the production of litharge goes on uninterruptedly until all the lead is removed. The button of silver is again fused in a smaller furnace, resting on a porous earthen dish, made with lixiviated wood-ashes, called a *test*, the porosity of which is so great, that it absorbs any remaining portions of litharge which may be formed on the silver.

The ores commonly employed in the process of amalgamation, which has been long used at Freyberg in Saxony, and is extensively practised in the silver and gold mines of South America, are native silver and its sulphuret. At Freyberg the ore in fine powder is mixed with sea-salt, and carefully roasted in a reverberatory furnace. The production of sulphuric acid leads to the formation of sulphate of soda, while the chlorine of the sea-salt combines with silver. The roasted mass is ground to a fine powder, and, together with mercury, water, and fragments of iron, is put into barrels, which are made to revolve by machinery. In this operation, intended to insure perfect contact between the materials, chloride of silver is decomposed by the iron, the silver unites with the mercury, and the chloride of iron is dissolved by the water. The mercury is then squeezed through leathern bags, the pores of which permit the pure mercury to pass, but retain the amalgam of silver. The combined mercury is then distilled off in close vessels, and the metals obtained in a separate state.

Goldsmith's silver commonly contains copper and traces of gold, the latter appearing in dark flocks when the metal is dissolved in nitric acid. It may be obtained pure for chemical uses by placing a clean piece of copper in a solution of nitrate of oxide of silver, washing the precipitate with pure water, and then digesting it in ammonia, in order to remove any adhering copper. A better process is to decompose chloride of silver by means of carbonate of potassa. For this purpose precipitate a solution of nitrate of oxide of silver with chloride of sodium, wash the precipitate with water, and dry it. Then put twice its weight of carbonate of potassa into a clean Hessian or black-lead crucible, heat it to redness, and throw the chloride by successive portions into the fused alkali. Effervescence takes place from the evolution of carbonic acid and oxygen gases, chloride of potassium is generated, and metallic silver subsides to the bottom. The pure metal may be granulated by pouring it while fused from a height of seven or eight feet into a vessel of water.

Silver has the clearest white colour of all the metals, and is susceptible of receiving a lustre surpassed only by polished steel. In malleability and ductility it is inferior only to gold, and its tenacity is considerable. It is very soft when pure, so that it may be cut with a knife. Its density after being hammered is 10.51. At a full red heat, corresponding to 1873° F., according to Mr. Daniell, it enters into fusion.

Pure silver does not rust by exposure to air and moisture. When fused in open vessels it absorbs oxygen in considerable quantity, amounting sometimes to 22 times its volume; but it parts with the whole of it in the act of becoming solid. This fact, first noticed by M. Lucas, has been studied by Gay-Lussac, who attributes to it the peculiarly beautiful aspect of granulated silver: he observed the absorption and subsequent evolution of oxygen to be most abundant in the purest silver, and is entirely prevented by a very small per-centage of copper. If silver is heated to redness, without fusing, in contact with glass or porcelain, it readily absorbs oxygen, and the oxide fuses with the earthy matters, forming a yellow enamel. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the ox-hydrogen blowpipe, it burns with vivid scintillations of a greenish-white colour.

The only pure acids that act on silver are the sulphuric and nitric acids, by both of which it is oxidized, forming with the first a sulphate, and with the second a nitrate of oxide of silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with its oxide a salt, which, after fusion, is known by the name of *lunar caustic.*

From recent experiments on the composition of the chloride and nitrate of the oxide of silver, I have deduced 108 as the equivalent of silver, an estimate closely corresponding with the previous researches of Berzelius. (Phil. Trans. 1833, part ii.) The compounds of silver described in this section are thus constituted:—

	Silver.			Equiv.	Formulæ.
Oxide	108	1 eq. + Oxygen	8	1 eq. = 116	$Ag+O$ or $\dot{Ag}$.
Chloride	108	1 eq. + Chlorine	35.42	1 eq. = 143.42	$Ag+Cl$ or $AgCl$.
Iodide	108	1 eq. + Iodine	126.3	1 eq. = 234.3	$Ag+I$ or AgI.
Sulphuret	108	1 eq. + Sulphur	16.1	1 eq. = 124.1	$Ag+S$ or AgS.
Cyanuret	108	1 eq. + Cyanogen	26.39	1 eq. = 134.39	$Ag+Cy$ or $AgCy$.

Oxide of Silver.—This oxide is best procured by mixing a solution of pure baryta with nitrate of oxide of silver dissolved in water. It is of a brown colour, insoluble in water, and is completely reduced by a red heat.

Silver is separated from its solution in nitric acid by pure alkalies and alkaline earths as the brown oxide, which is redissolved by ammonia in excess; by alkaline carbonates as a white carbonate, which is soluble in an excess of carbonate of ammonia; as a dark brown sulphuret by hydrosulphuric acid; and as a white curdy chloride of silver, which is turned violet by light and is very soluble in ammonia, by hydrochloric acid or any soluble chloride. By the last character, silver may be both distinguished and separated from other metallic bodies.

Silver is precipitated in the metallic state by most other metals. When mercury is employed for this purpose, the silver assumes a beautiful arborescent appearance, called *arbor Dianæ.* A very good proportion for the experiment is twenty grains of lunar caustic to six drachms or an ounce of water. The silver thus deposited always contains mercury.

When oxide of silver, recently precipitated by baryta or lime-water, and separated from adhering moisture by bibulous paper, is left in contact for ten or twelve hours with a strong solution of ammonia, the greater part of it is dissolved; but a black powder remains which detonates violently from heat or percussion. This substance, which was discovered by Berthollet, (An. de Chimie, i.) appears to be a compound of ammonia and oxide of silver; for the products of its detonation are metallic silver, water, and nitrogen gas. It should be made in very small quantity at a time, and dried spontaneously in the air.

On exposing a solution of oxide of silver in ammonia to the air, its surface becomes covered with a pellicle, which Faraday considers to be an oxide containing a smaller proportion of oxygen than that just described. This opinion he has made highly probable; but further experiments are requisite before the existence of this oxide can be regarded as certain.

Chloride of Silver.—This compound, which sometimes occurs in silver mines, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing hydrochloric acid, or any soluble chloride, with a solution of nitrate of oxide of silver. As formed by precipitation it is quite white; but by exposure to the direct solar rays it becomes violet, and almost black, in the course of a few minutes; and a similar effect is slowly produced by diffused day-light. Hydrochloric acid is set free during this change, and, according to Berthollet, the dark colour is owing to separation of oxide of silver. (Statique Chimique, vol. i. p. 195.)

Chloride of silver, sometimes called *horn silver*, is insoluble in water, and is dissolved very sparingly by the strongest acids; but it is soluble in ammonia. Hyposulphurous acid likewise dissolves it. At a temperature of about 500° it fuses, and forms a semi-transparent horny mass on cooling, which has a density of 5.524. It bears any degree of heat, or even the combined action of pure charcoal and heat, without decomposition; but hydrogen gas decomposes it readily with formation of hydrochloric acid.

Iodide of Silver.—This compound is formed when iodide of potassium is mixed with a solution of nitrate of oxide of silver. It is of a greenish-yellow colour, and is insoluble in water and ammonia.

Cyanuret of Silver is formed by mixing hydrocyanic acid with nitrate of oxide of silver. It is a white curdy substance, similar in appearance to chloride of silver, insoluble in water, but soluble in a solution of ammonia and in hot nitric acid. It is decomposed by hydrochloric acid with formation of hydrocyanic acid and chloride of silver.

Sulphuret of Silver.—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing hydrosulphuric acid gas, owing to the formation of a sulphuret. On transmitting a current of this gas through a solution of lunar caustic, a dark brown precipitate subsides, which is a sulphuret of silver. The *silver glance* of mineralogists is a similar compound, and the same sulphuret may be prepared by heating thin plates of silver with alternate layers of sulphur. This sulphuret is remarkable for being soft and even malleable.

Silver unites also by the aid of heat with phosphorus, forming a soft, brittle, crystalline compound.

SECTION XXVI.

GOLD.

Gold appears to have been known to the earliest races of man, and to have been esteemed by them as much as by the moderns. It has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallizes in octohedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial depositions, especially among sand in the beds of rivers, having been washed by water out of disintegrated rocks in which it originally existed. There are few countries in which gold washings have not formerly existed; but the principal supply of gold is from South America, from the gold mines of Hungary, and from the Uralian mountains of Siberia, especially on the Asiatic side of the chain, where separate masses in sand have been found weighing 18 or 20 pounds. Rich deposites of gold appear also to exist in some of the southern provinces of North America. Gold is generally separated from accompanying impurities by the process of amalgamation, similar to that described in the last section; by which means it is freed from iron and all associated metals, excepting silver. In Hungary the gold is purified by cupellation. The silver, which in variable quantity is present in native gold, may be brought into view by dissolving the gold in nitro-hydrochloric acid. The best mode of separation consists in fusing the gold with so much silver that the former may constitute one-fourth of the mass: nitric acid will then dissolve all the silver, and leave the gold. The silver may also be removed by digestion in sulphuric acid.

Gold is the only metal which has a yellow colour, a character by which it is distinguished from all other simple metallic bodies. It is capable of receiving a high lustre by polishing, but is inferior in brilliancy to steel, silver, and mercury. In ductility and malleability it exceeds all other metals; but it is surpassed by several in tenacity. Its density is 19.257; when pure it is exceedingly soft and flexible; and it fuses according to Mr. Daniell at 2016° F.

Gold may be exposed for ages to air and moisture without change, nor is it oxidized by being kept in a state of fusion in open vessels. When intensely ignited by means of electricity or the oxy-hydrogen blowpipe, it burns with a greenish-blue flame, and is dissipated in the form of a purple powder, which is supposed to be an oxide.

Gold is not oxidized or dissolved by any of the pure acids; for it may be boiled even in nitric acid without undergoing any change. Its best solvents are chlorine and nitro-hydrochloric acid; and it appears from the observations of Davy that chlorine is the agent in both cases, since nitro-hydrochloric acid does not dissolve gold, except when it gives rise to the formation of chlorine. (Page 215.) It is to be inferred, therefore, that the chlorine unites directly with the gold.

The most convenient method of dissolving it, is to digest fragments of the metal in a mixture composed of two measures of hydrochloric and one of nitric acid, until the acid is saturated. The excess of acid is then expelled by evaporating the orange-coloured solution until a ruby-red liquid remains, which is the neutral terchloride of gold. On adding water, the chloride is dissolved, forming a solution of a gold-yellow colour.

The equivalent of gold, estimated from the analysis of the terchloride by Berzelius, is 199.2. The composition of its compounds described in this section is as follows:—

	1 eq. Gold.		Equiv.	Formulæ.
Protoxide	199.2 + Oxygen	8	1 eq.=207.2	$Au+O$ or $\dot{Au}$.
Binoxide	199.2 + do.	16	2 eq.=215.2	$Au+2O$ or $\ddot{Au}$.
Peroxide	199.2 + do.	24	3 eq.=223.2	$Au+3O$ or $\dddot{Au}$.
Protochloride	199.2 + Chlorine	35.42	1 eq.=234.62	$Au+Cl$ or $AuCl$.
Terchloride	199.2 + do.	106.26	3 eq.=305.46	$Au+3Cl$ or $AuCl^3$.
Tersulphuret	199.2 + Sulphur	48.3	3 eq.=247.5	$Au+3S$ or AuS^3.

Protoxide of Gold.—It is obtained by the action of a cold solution of potassa on the protochloride of gold, and is separated as a green precipitate, which is partially soluble in the alkaline solution. It spontaneously changes soon after its preparation into metallic gold and the peroxide.

The *binoxide* is supposed to be the purple oxide which is formed by the combustion of gold: but its composition has not been demonstrated by analysis.

Peroxide.—This, the only well-known oxide of gold, is prepared by the action of alkalies on the terchloride, but is obtained quite pure with difficulty. Pelletier recommends that it should be formed by digesting a solution of the terchloride with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid. It is apt, however, to retain magnesia, and I am informed by Dr. Wagner, of Pesth in Hungary, that the most certain mode of procuring the peroxide is the following. Dissolve 1 part of gold in the usual way, render it quite neutral by evaporation, and redissolve in 12 parts of water: to the solution add 1 part of carbonate of potassa dissolved in twice its weight of water, and digest at about 170°. Carbonic acid gradually escapes, and the hydrated peroxide of a brownish-red colour subsides. After being well washed it is dissolved in colourless nitric acid of specific gravity 1.4, and the solution decomposed by admixture with water. The hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by a temperature of 212° F.

Peroxide of gold is yellow in the state of hydrate, and nearly black when anhydrous, is insoluble in water, and completely decomposed by solar light or a red heat. Hydrochloric acid dissolves it readily, yielding the common solutions of gold; but it forms no definite compound with any acid which contains oxygen. It may indeed be dissolved by nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. This property, which constitutes the difficulty of procuring peroxide of gold quite pure, induced Pelletier to deny that the peroxide of gold is a salifiable base, and to propose for it the name of *auric acid*, its compounds with alkalies being called *aurates*. (An. de Ch. et de Ph. xv.)

When recently precipitated peroxide of gold is kept in strong ammonia for about a day, a detonating compound of a deep olive colour is generated, analogous to the fulminating silver described in the last section. According to the analysis of Dumas, its elements are in the ratio of one equivalent of gold, two of nitrogen, six of hydrogen, and three of oxygen, as expressed by the symbols $Au+2N+6H+3O$. With regard to the mode in which these elements are arranged, different opinions may be formed. Dumas thinks the real combination is indicated by the formula $(Au+N)+(3H+N)+3\dot{H}$, being a hydrated nituret of gold united with ammonia; but it appears more simple to consider it as a diaurate of ammonia, expressed by the formula $2(3H+N)+\dddot{Au}$. Its detonation should give rise to metallic gold, water, nitrogen, and ammonia. A similar compound is obtained, and this is the ordinary mode of procuring fulminating gold, by digesting terchloride of gold with an excess of ammonia: a yellow precipitate subsides, the fulminating ingredient of which appears identical with that above described; but a subchloride of gold and ammonia falls at the same time, and adheres so obstinately that it cannot be wholly removed by boiling water. Fulminating gold may be dried at 212°; but friction, or a heat suddenly raised to about 290° or upwards, produces a violent detonation. It is best to make it in small quantities at a time, and to dry it in the open air. (An. de Ch. et de Ph. xliv. 167.)

Chlorides of Gold. On concentrating the solution of gold to a sufficient extent by evaporation, the *terchloride* may be obtained in ruby-red prismatic crystals, which are very fusible. It deliquesces on exposure to the air, and is dissolved readily by water without residue. It is also soluble in alcohol and ether; and the latter withdraws it from the aqueous solution. It begins to lose chlorine at a temperature of about 400°, being changed into a brown dry mass, which is a mixture of the *protochloride* and terchloride, soluble in water. At about 600° the terchloride is completely resolved into the yellow insoluble protochloride, which by boiling in water is changed into metallic gold and the soluble terchloride. At a red heat the protochloride loses its chlorine altogether, and metallic gold remains.

The terchloride of gold, is the usual and most convenient form of obtaining a solution of gold, and examining its properties in that state. On adding to the solution sulphate of protoxide of iron, a brown precipitate ensues, which is gold in very fine division, and the solution contains sesquisulphate of peroxide, and perchloride of iron. The action is such that

6 eq. sulphate of protoxide of iron	$6(\dot{Fe}+\dddot{S})$
and 1 eq. terchloride of gold	$Au+3Cl$

yield

2 eq. tersulphate of peroxide of iron	$2(\overset{\cdots}{Fe}+3\dddot{S})$
1 eq. perchloride of iron	$2Fe+3Cl.$
and 1 eq. gold	$Au.$

The precipitate, when duly washed with dilute hydrochloric acid in order to separate adhering iron, is gold in a state of prefect purity. A similar reduction is effected by most of the metals, and by sulphurous and phosphorous acids, and by oxalic acid with escape of carbonic acid gas. When a piece of charcoal is immersed in a solution of gold, and exposed to the direct solar rays, its surface acquires a coating of metallic gold, and ribands may be gilded by moistening them with a dilute solution of gold, and exposing them to a current of hydrogen or phosphuretted hydrogen gas. When a strong aqueous solution of gold is shaken in a phial with an equal volume of pure ether, two fluids result, the lighter of which is an ethereal solution of gold. From this liquid flakes of metal are deposited on standing, especially by exposure to light, and substances moistened with it receive a coating of metallic gold.* The reduction in most of these instances is owing to the chlorine quitting the gold in obedience to some stronger attraction: metals deprive it directly of its chlorine; and deoxidizing agents do so indirectly by combining with the oxygen of water, while the hydrogen acts on the chlorine.

When protochloride of tin is added to a dilute aqueous solution of gold, a purple-coloured precipitate, called the *purple of Cassius*, is thrown down; and the same substance may be prepared by fusing together 150 parts of silver, 20 of gold, and 35.1 of tin, and acting on the alloy with nitric acid, which dissolves out the silver and leaves a purple residue, containing the tin and gold which were employed. To prevent the oxidation of the tin during fusion, the three metals should be projected into a red-hot black-lead crucible, which contains a little melted borax. When the powder of Cassius is fused with vitreous substances, such as flint-glass, or a mixture of sand and borax, it forms with them a purple enamel, which is employed in giving pink colours to porcelain. The essential cause of the colour is probably a compound of the purple or supposed binoxide of gold with earthy matters, similar to the enamel formed by glass and oxide of silver: the oxide of tin is not essential, since finely divided metallic gold alone will give the same tint of purple.

The chemical nature of the purple of Cassius is very obscure. From its formation by protochloride of tin, it is inferred to contain peroxide of tin, and gold either in the metallic state or oxidized to a degree inferior to the peroxide. According to Berzelius, its sole loss when heated to redness is

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* With respect to the revival of gold from its solutions, the reader may consult an Essay on Combustion by Mrs. Fulhame, and a paper by Count Rumford in the Philosophical Transactions for 1798.

7.65 per cent. of water, and the residue has a brick-red colour arising from a mechanical mixture of metallic gold and peroxide of tin, a statement which is confirmed by Gay-Lussac. (An. de Ch. et de Ph. xlix. 396.) The proportion of these products corresponds to six equivalents of peroxide of tin, one of gold, and six of water. Nevertheless, the purple of Cassius, as is indicated both by its colour and its solubility in ammonia, is not a mechanical mixture of these ingredients; nor can it well be regarded as a chemical compound of gold and peroxide of tin, since no definite compound of the kind is known to chemists. The more probable supposition is, that it is a hydrated double salt, composed of peroxide of tin as the acid, united with protoxide of tin and binoxide of gold as bases, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin. A compound of this nature is expressed by the formula $2(\dot{S}n + \ddot{S}n) + (\ddot{A}u + \ddot{S}n) + 6\dot{H}$.

Tersulphuret of Gold.—On transmitting a current of hydrosulphuric acid gas through a solution of gold, a black precipitate is formed, which is the tersulphuret. It is resolved by a red heat into gold and sulphur.

The compounds of gold with the other non-metallic bodies have been little examined.

SECTION XXVII.

PLATINUM.

This valuable metal occurs only in the metallic state, associated or combined with various other metals, such as copper, iron, lead, titanium, chromium, gold, silver, palladium, rhodium, osmium, and iridium. It has hitherto been found chiefly in Brazil, Peru, and other parts of South America, in the form of rounded or flattened grains of a metallic lustre and white colour, mixed with sand and other alluvial depositions. The particles rarely occur so large as a pea; but they are sometimes larger, and a specimen brought from South America by Humboldt was rather larger than a pigeon's egg, and weighed 1088.6 grains. In the year 1826, however, Boussingault discovered it in a syenitic rock in the province of Antioquia in South America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been discovered in the Uralian Mountains. (Edinburgh Journal of Science, v. 323.)

Pure platinum has a white colour very much like silver, but of inferior lustre. It is the heaviest of known metals, its density after forging being about 21.25, and 21.5 in the state of wire. Its malleability is considerable, though far less than that of gold and silver. It may be drawn into wires, the diameter of which does not exceed the 2000th part of an inch. It is a soft metal, and like iron admits of being welded at a high temperature. Dr. Wollaston* observed that it is a less perfect conductor of heat than several other metals.

Platinum undergoes no change from the combined agency of air and moisture; and it may be exposed to the strongest heat of a smith's forge without suffering either oxidation or fusion. On heating a small wire of it by means of galvanism or the oxy-hydrogen blowpipe, it is fused, and afterwards burns with the emission of sparks. Smithson Tennant showed that it is oxidized when ignited with nitre (Philos. Trans. 1797); and a similar effect is occasioned by pure potassa and lithia. It is not attacked by any of the pure acids. Its solvents are chlorine, or solutions, such as nitro-hydrochloric acid, which supply chlorine; and it is dissolved with greater difficulty than gold.

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* The reader will find, in the Philosophical Transactions for 1829, some important directions by Dr. Wollaston, both as to the mode of extracting platinum from its ores, and of communicating to the pure metal its highest degree of malleability. The essay receives additional interest, from being one of those which were composed during the last illness of this truly illustrious philosopher.

The remarkable property observed by Döbereiner in spongy platinum of causing the union of oxygen and hydrogen gases, was mentioned at page 159, a property which Dulong and Thenard showed to be also possessed, though in a lower degree, by platinum in its compact form of wire or foil, and by several other metals. (An. de Ch. et de Ph. xxiii. and xxiv.) Faraday (Phil. Trans. 1834, part i.) has lately discussed, with his wonted ability and success, both the conditions required for the effective action of platinum, and the cause of the phenomenon. The sole conditions are purity of the gases, and perfect cleanliness of the platinum. By cleanliness is meant perfect absence of foreign matter, pure water excepted, and this condition is easily secured by fusing pure potassa on its surface, washing off the alkali by pure water, then dipping the platinum in hot oil of vitriol, and again washing with water. In this state platinum foil acts so rapidly at common temperatures on oxygen and hydrogen gases mixed in the ratio of 1 to 2, that it often becomes red-hot and kindles the mixture. Handling the platinum, wiping it with a towel, or exposing it to the atmosphere for a few days, suffices to soil the surface of the metal, and thereby diminish or prevent its action. These phenomena are supposed to result from the concurring influence of two forces, the self-repulsive energy of similar gaseous particles, and the adhesive attraction exerted between them and the platinum. Each gas, repulsive to itself and not repelled by the platinum, comes into the most intimate contact with that metal, and both gases are so condensed upon its surface, that they are brought within the sphere of their mutual attraction and combine. Faraday has given several instances, similar to those which I had occasion to describe some years ago (Jameson's Journal, xi. 99 and 311), where the action of platinum is retarded or altogether prevented by small quantities of certain gases, such as hydrosulphuric acid, carbonic oxide, and olefiant gases. One would be tempted to suppose that these gases act by soiling the metallic surface, though in some respects this explanation is not satisfactory.

The equivalent of platinum, deduced by Berzelius from the analysis of the bichloride, is 98.8. The composition of its compounds described in this section is as follows:—

	Platinum.		Equiv.	Formulæ.
Protoxide	98.8 1 eq.+Oxygen	8	1 eq.=106.8	Pl+O or $\dot{\text{Pl}}$.
Binoxide	98.8 1 eq.+do.	16	2 eq.=114.8	Pl+2O or $\ddot{\text{Pl}}$.
Sesquioxide?	197.6 2 eq.+do.	24	3 eq.=221.6	2Pl+3O or $\dddot{\overline{\text{Pl}}}$.
Protochloride	98.8 1 eq.+Chlorine	35.42	1 eq. =134.22	Pl +Cl or PlCl.
Bichloride	98·8 1 eq.+do.	70·84	2 eq.=169.64	Pl+2Cl or PlCl^2.
Protiodide	98.8 1 eq.+Iodine	126.3	1 eq.=225.1	Pl+I or PlI.
Biniodide	98·8 1 eq.+do.	252·6	2 eq.=351.4	Pl+2I or PlI^2.
Protosulphuret	98.8 1 eq.+Sulphur	16.1	1 eq.=114.9	Pl+S or PlS.
Bisulphuret	98.8 1 eq.+do.	32.2	2 eq.=131	Pl+2S or PlS^2.

Protoxide of Platinum.—This oxide is prepared by digesting protochloride of platinum in a solution of pure potassa, avoiding a large excess of the alkali, since it dissolves a portion of the oxide, and thereby acquires a green colour. In this state it is a hydrate which loses first its water and the-oxygen when heated, and dissolves slowly in acids, yielding solutions of a brownish-green tint.

Binoxide.—This oxide is prepared with difficulty, owing to its disposition, like peroxide of gold, to act rather as an acid than an alkaline base, and either to fall in combination with any alkali by which it is precipitated, or to remain with it altogether in solution. Berzelius recommends that it should be prepared by exactly decomposing sulphate of binoxide of platinum with nitrate of baryta, and adding pure soda to the filtered solution, so as to precipitate about half of the oxide; since otherwise, a sub-salt would subside. The oxide falls in the form of a bulky hydrate, of a yellowish-brown colour: it resembles rust of iron when dry, and is nearly black when rendered anhydrous.

Sesquioxide.—This oxide, of a gray colour, is prepared, according to its discoverer Mr E. Davy, by heating fulminating platinum with nitrous acid; but the nature of the compound so formed has not yet been decisively determined. (Phil. Trans. 1820.)

Protochloride.—When the bichloride is heated to 450°, half of its chlorine is expelled, and the protochloride of a greenish-gray colour remains. It is insoluble in water, sulphuric acid, and nitric acid; but hydrochloric acid partially dissolves it, yielding a red solution. At a red heat its chlorine is driven off, and metallic platinum is left. It is dissolved by a solution of the bichloride.

Bichloride of Platinum.—This chloride is obtained by evaporating the solution of platinum in nitro-hydrochloric acid to dryness at a very gentle heat, when it remains as a red hydrate, which becomes brown when its water is expelled. It is deliquescent, and very soluble in water, alcohol, and ether; its solution, if free from the chlorides of palladium and iridium, being of a pure yellow colour. Its ethereal solution is decomposed by light, metallic platinum being deposited.

A solution of platinum is recognized by the following characters. When to an alcoholic or concentrated aqueous solution of the bichloride, a solution of chloride of potassium is added, a crystalline double chloride of a pale yellow colour subsides, which is insoluble in alcohol, and sparingly soluble in water: at a red heat it yields chlorine gas, and the residue consists of metallic platinum and chloride of potassium. With a solution of hydrochlorate of ammonia a similar yellow salt falls, which when ignited leaves pure platinum in the form of a delicate spongy mass, the power of which in kindling an explosive mixture of oxygen and hydrogen gases has already been mentioned.

Protiodide of Platinum.—Lassaigne prepared this compound by digesting the protochloride of platinum in a rather strong solution of iodide of potassium, when the protiodide gradually appeared in the form of a black powder, which is insoluble in water and alcohol. It is unchanged by the sulphuric, nitric, and hydrochloric acids, decomposed by the alkalies, and at a red heat gives off its iodine.

Biniodide of Platinum.—Lassaigne prepares this compound by the action of iodide of potassium on a rather dilute solution of bichloride of platinum. At first the liquid acquires an orange-red and then a claret colour, without any precipitation; but when the solution is boiled, a black precipitate subsides, which should be washed with hot water and dried at a heat not exceeding 212°. This biniodide is a black powder, sometimes crystalline, is tasteless and inodorous, insoluble in water, and may be boiled in water without change. By alcohol it is sparingly dissolved, especially when heated. Acids act feebly upon it; but it is decomposed by alkalies, and begins to lose iodine at 270°. (An. de Ch. et de Ph. li. 113.)

Protosulphuret of Platinum.—It is formed by heating in a retort the yellow ammoniacal chloride of platinum with half its weight of sulphur until all the salammoniac and excess of sulphur are expelled. The protosulphuret is then left as a gray powder of a metallic lustre. It may also be formed by the action of hydrosulphuric acid on protochloride of platinum.

Persulphuret.—It is formed as a brown precipitate, which becomes black when dried, by letting fall a solution of bichloride of platinum drop by drop into a solution of sulphuret of potassium, or by transmitting hydrosulphuric acid gas into a solution of the double chloride of platinum and sodium. (Berzelius.) It should be dried in vacuo by aid of sulphuric acid; since, by exposure to the air in a moist state, sulphuric acid is generated.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of sulphate of oxide of platinum. (E. Davy.) It is analogous to the detonating compounds which ammonia forms with the oxides of gold and silver.

SECTION XXVIII.

PALLADIUM, RHODIUM, OSMIUM, AND IRIDIUM.

The four metals to be described in this section are all contained in the ore of platinum, and have hitherto been procured in very small quantity. When the ore is digested in nitro-hydrochloric acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left consisting of osmium and iridium.

PALLADIUM.

This metal was discovered in 1803 by Wollaston (Phil. Trans. 1804 and 1805). On adding bicyanuret of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by hydrochlorate of ammonia, a yellowish-white flocculent precipitate is gradually deposited, which is cyanuret of palladium. When this compound is heated to redness, the cyanogen is expelled, and pure palladium remains. In order to obtain it in a malleable state, the metal should be heated with sulphur, and the resulting sulphuret purified by cupellation in an open crucible with borax and a little nitre. It is then roasted at a low red heat on a flat brick, and when reduced to a pasty consistence, it is pressed into a square or oblong perfectly flat cake. It is again to be roasted very patiently, at a low red heat, until it becomes spongy on the surface; and when quite cold, it is condensed by frequent tappings with a light hammer. By alternate roastings and tappings the sulphur is burned off, and the metal rendered sufficiently dense to be laminated. Thus prepared it is rather brittle while hot, which Wollaston supposed to arise from a small remnant of sulphur. (Phil. Trans. 1829, p. 7.)

Palladium resembles platinum in colour and lustre. It is ductile as well as malleable, and is considerably harder than platinum. Its specific gravity varies from 11.3 to 11.8. In fusibility it is intermediate between gold and platinum, and is dissipated in sparks when intensely heated by the oxy-hydrogen blowpipe. At a red heat in oxygen gas, its surface acquires a fine blue colour, owing to superficial oxidation; but the increase of weight is so slight as not to be appreciated.

Palladium is oxidized and dissolved by nitric acid, and even the sulphuric and hydrochloric acids act upon it by the aid of heat; but its proper solvent is nitro-hydrochloric acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by sulphate of protoxide of iron, and by all the metals described in the foregoing sections, excepting silver, gold, and platinum.

From the analysis by Berzelius of the double chloride of palladium and potassium the equivalent of palladium is inferred to be 53.3. The composition of its compounds described in this section is as follows:—

	Palladium.				Equiv.	Formulæ.
Protoxide	53.3	1 eq. + Oxyg.	8	1 eq. =	61.3	$Pd+O$ or $\dot{Pd}$.
Binoxide	53.3	1 eq. + do.	16	2 eq. =	69.3	$Pd+2O$ or $\ddot{Pd}$.
Protochloride	53.3	1 eq. + Chlor.	35.42	1 eq. =	88.72	$Pd+Cl$ or $PdCl$.
Bichloride	53.3	1 eq. + do.	70.84	2 eq. =	124.14	$Pd+2Cl$ or $PdCl^2$.
Protosulphuret	53.3	1 eq. + Sulph.	16.1	1 eq. =	69.4	$Pd+S$ or PdS.

Protoxide of Palladium.—This oxide is obtained as a hydrate of a deep brown colour by decomposing its salts with an excess of carbonate of potassa or soda; and, by washing and heating to low redness, the anhydrous protoxide of a black colour is left. It is also obtained by heating the nitrate at a low red heat. In the anhydrous state it is dissolved with difficulty by acids. When strongly heated it parts with its oxygen. Berzelius says it falls from its salts on the addition of the alkalies as a subsalt, which is dissolved by the alkali in excess.

Binoxide.—To prepare this oxide Berzelius recommends that a solution of potassa or its carbonate in excess should be poured by little and little on the *solid* bichloride of palladium and potassium, and the materials be well intermixed: water is not first added, because it decomposes the double chloride; and the alkali is not added all at once, because the binoxide would then be dissolved at first, and afterwards separate out as a gelatinous hydrate, which could not be purified by washing. When prepared with the foregoing directions, the binoxide is obtained as a hydrate of a deep yellowish-brown colour, which retains a little potassa in combination; but on heating the solution to 212°, the alkali is dissolved and the anhydrous black oxide left.

Protochloride of Palladium.—It is obtained by evaporating to dryness a solution of palladium in nitro-hydrochloric acid, being left as a brown crystalline hydrate, which becomes black when its water is expelled. It loses its chlorine when strongly heated, and is soluble in water.

The *bichloride* is formed by digesting the protochloride in nitro-hydrochloric acid, and exists only in solution, the colour of which is of so deep a brown as to appear nearly black. It is readily distinguished from the protochloride by yielding with chloride of potassium a double chloride of a red colour; whereas that formed with the protochloride is yellow.

Protosulphuret of Palladium.—It is readily formed by heating the metal with sulphur, and is a fusible brittle compound of a gray colour.

RHODIUM.

This metal was discovered by Wollaston at the time he was occupied with the discovery of palladium. On immersing a thin plate of clean iron into the solution from which palladium and the greater part of the platinum have been precipitated, the rhodium, together with small quantities of platinum, copper, and lead, is thrown down in the metallic state; and on digesting the precipitate in dilute nitric acid, the two last metals are removed. The rhodium and platinum are then dissolved by means of nitro-hydrochloric acid, and the solution, after being mixed with some chloride of sodium, is evaporated to dryness. Two double chlorides result, that of platinum and sodium, and of rhodium and sodium, the former of which is soluble, and the latter insoluble in alcohol; and they may, therefore, be separated from each other by this menstruum. The double chloride of rhodium is then dissolved in water, and metallic rhodium precipitated by insertion of a rod of zinc.

Rhodium, thus procured, is in the form of a black powder, which requires the strongest heat that can be produced in a wind furnace for fusion, and when fused has a white colour and metallic lustre. It is brittle, is extremely hard, and has a specific gravity of about 11. It attracts oxygen at a red heat, a mixture of peroxide and protoxide being formed. It is not attacked by any of the acids when in its pure state; but if alloyed with other metals, such as copper or lead, it is dissolved by nitro-hydrochloric acid, a circumstance which accounts for its presence in the solution of crude platinum. It is oxidized by being ignited either with nitre, or bisulphate of potassa. When heated with the latter, sulphurous acid gas is evolved, and a double sulphate of peroxide of rhodium and potassa is generated, which dissolves readily in hot water, and yields a yellow solution. The presence of rhodium in platinum, iridium, and osmium may thus be detected, and by repeated fusion a perfect separation be accomplished. (Berzelius.)

Chemists are acquainted with two oxides of rhodium. The protoxide is black, and the peroxide, which is the base of the salts of rhodium, is of a yellow colour. Most of its salts are either red or yellow.

From the composition of the double chloride of rhodium and potassium Berzelius considers 52.2 as the equivalent of rhodium; and its compounds described in this section are thus constituted:—

	Rhodium.					Equiv.	Formulæ.
Protoxide	52.2	1 eq. +	Oxygen	8	1 eq. =	60.2	$R + O$ or $\dot{R}$.
Peroxide	104.4	2 eq. +	do.	24	3 eq. =	128.4	$2R + 3O$ or $\dddot{R}$.
Protochloride	52.2	1 eq. +	Chlor.	35.42	1 eq. =	87.62	$R + Cl$ or $\overline{RCl}$.
Perchloride	104.4	2 eq. +	do.	106.26	3 eq. =	210.66	$2R + 3Cl$ or R^2Cl^3.
Sulphuret.	Probably a protosulphuret.						

Oxides of Rhodium.—The first grade of oxidation has not yet been insulated. The *peroxide* is generated when pulverulent rhodium is heated to redness in a silver crucible mixed with hydrate of potassa and a little nitre, when the rhodium is oxidized and acquires a coffee-brown colour. To remove the potassa united with the peroxide, the mass is first washed with water and then digested in hydrochloric acid, when it acquires a greenish-gray colour, and is left as a pure hydrate of the peroxide. In this state it is insoluble in acids. If an excess of carbonate of potassa or soda is added to the double chloride of rhodium and potassium, and the solution is evaporated, a gelatinous hydrate falls; but on attempting to dissolve in acid the potassa combined with the peroxide, the latter is also dissolved.

Chlorides of Rhodium.—The only chloride which has yet been insulated is the *perchloride*, which Berzelius obtained by adding to a solution of the double chloride of rhodium and potassium, silico-hydrofluoric acid as long as the double fluoride of potassium and silicium was generated, after which the filtered liquid was evaporated to dryness, and redissolved in water. This perchloride when dry has a dark brown colour, is uncrystalline, and decomposed by a full red heat into chlorine and metallic rhodium. It deliquesces in the air into a brown liquid, and its aqueous solution has a fine red colour, whence its name of rhodium (from ῥόδον, a rose) is derived. (An. de Ch. et de Ph. xl. 51.

Sulphuret of Rhodium.—It may be formed by heating rhodium directly with sulphur, fuses at a white heat without decomposition, and has a bluish-gray colour with a metallic lustre. Wollaston made use of it for procuring the metal in a coherent state, in the same manner as sulphuret of palladium

OSMIUM AND IRIDIUM.

These metals were discovered by the late Mr. Tennant in the year 1803 (Phil. Trans. 1804), and the discovery of iridium was made about the same time by M. Descotils in France. The black powder mentioned at the beginning of this section is a compound of osmium and iridium, an alloy which Wollaston detected in the form of flat white grains among fragments of crude platinum. This alloy, which is quite insoluble in nitro-hydrochloric acid, is the source from which osmium and iridium are extracted.

Osmium.—This metal is separated from the alloy just mentioned by fusion with soda or nitre; and the following process, given by Wollaston, may be resorted to with advantage. (Phil. Trans. 1829, p. 8.) The pulverulent alloy is ground into a fine powder with a third of its weight of nitre, and the mixture heated to redness in a silver crucible until it is reduced to a pasty state, when the characteristic odour of oxide of osmium will be perceptible. Dissolve the soluble parts, which contain oxide of osmium in combination with potassa, in the smallest possible quantity of water, and acidulate the solution, introduced into a retort, with sulphuric acid diluted with its own weight of water. By distilling rapidly into a clean receiver as long as osmic fumes pass over, the oxide will be collected on its sides in the form of a white crust; and, there melting, it will run down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. As the receiver cools the oxide becomes solid and crystallizes.

Osmium is precipitated from the solution of its oxide by all the metals excepting gold and silver. A convenient mode of reduction is to agitate it with mercury, adding hydrochloric acid to decompose the protoxide of mercury which is formed, and then expelling the mercury and calomel by heat. The osmium is left as a black porous powder, which acquires metallic lustre by friction. If it has been exposed to a very gentle heat, its specific gravity is 7, it takes fire when heated in the open air, and is readily oxidized and dissolved by fuming nitric acid; but a red heat gives it greater compactness, and in that state it ceases to be attacked by acids, and may be freely heated without oxidation. In its densest state Berzelius found its specific gravity to be 10. (An. de Ch. et de Ph. xl. 257, and xlii. 185.)

Berzelius, from his late researches on the compounds of osmium, considers 99.7 to be its equivalent, and gives the composition of its oxides, chlorides, and sulphurets as follows:—

	Osmium.			Equiv.	Formulæ.
Protoxide	99.7	1 eq.+Oxygen	8	1 eq.=107.7	Os+O or $\dot{Os}$.
Sesquioxide	199.4	2 eq.+do.	24	3 eq.=223.4	2Os+3O or $\underline{\dddot{Os}}$.
Binoxide	99.7	1 eq.+do.	16	2 eq.=115.7	Os+2O or $\ddot{Os}$.
Teroxide	99.7	1 eq.+do.	24	3 eq.=123.7	Os+3O or $\dddot{Os}$.
Peroxide	99.7	1 eq.+do.	32	4 eq.=131.7	Os+4O or $\ddddot{Os}$.
Protochlor.	99.7	1 eq.+Chlor.	35.42	1 eq.=135.12	Os+Cl or OsCl.
Sesquichlor.	199.4	2 eq.+do.	106.26	3 eq.=305.66	2Os+3Cl or Os^2Cl^3.
Bichloride	99.7	1 eq.+do.	70.84	2 eq.=170.54	Os+2Cl or $OsCl^2$.
Terchloride	99.7	1 eq.+do.	106.26	3 eq.=205.96	Os+3Cl or $OsCl^3$.
Protosulph.	99.7	1 eq.+Sulph.	16.1	1 eq.=115.8	Os+S or OsS.
Sesquisulph.	199.4	2 eq.+do.	48.3	3 eq.=247.7	2Os+3S or Os^2S^3.
Bisulphuret	99.7	1 eq.+do.	32.2	2 eq.=131.9	Os+2S or OsS^2.
Tersulph.	99.7	1 eq.+do.	48.3	3 eq.=148	Os+3S or OsS^3.

Oxides of Osmium.—For a minute description of these compounds I refer to the essays of Berzelius above cited. The *protoxide* is precipitated by pure alkalies from the protochloride, and falls as a deep green, nearly black, hydrate, which is soluble in acids, and detonates when heated with combustible matter. The *binoxide* is thrown down as a hydrate of deep brown colour when a saturated solution of the bichloride is heated with carbonate of soda. It retains a little alkali in combination; but the soda is easily removed by dilute hydrochloric acid, without the oxide being dissolved. The *teroxide* is prepared in like manner from the terchloride. The *sesquioxide* has not been obtained in a separate state; but it is procured in combination with ammonia, when the binoxide is treated with a large excess of pure ammonia, nitrogen gas being disengaged at the same time.

The highest stage of oxidation is the volatile oxide, which is the product of the oxidation of osmium by acids, by combustion, or by fusion with nitre or alkalies; and it may be procured by the process above mentioned in colourless transparent elongated crystals, or as a colourless solution in water. Its vapour is very acrid, exciting cough, irritating the eyes, and producing a copious flow of saliva; and its odour is disagreeable and pungent, somewhat like that of chlorine; a property which suggested the name of *osmium*. (From ὀσμῆ, odour.) It does not combine with acids; on the contrary, though it has no acid reaction, it unites with alkalies, and the compound sustains a strong heat without decomposition. It is hence sometimes called *osmic acid*. When touched, it communicates a stain which cannot be removed by washing. With the infusion of gall-nuts it yields a purple solution, which afterwards acquires a deep blue tint; a character which forms a sure and extremely delicate test for peroxide of osmium. By sulphurous acid it is deoxidized, and the colour of the solution passes through the shades of yellow, orange, brown, green, and lastly blue, when it resembles sulphate of indigo. These changes correspond to sulphates of the different oxides of osmium, the last or blue oxide being a compound of protoxide and sesquioxide of osmium.

Chlorides of Osmium.—Berzelius has described four chlorides of osmium, corresponding to the four first degrees of oxidation above mentioned. When osmium is heated in a tube in a current of dry chlorine gas, a deep green sublimate is formed, which is the protochloride. On continuing the process it yields a red sublimate, which is the bichloride. For the remaining details, which are rather minute, I may refer to the essay already cited. Several of these chlorides yield double compounds with sodium, potassium, and ammonia.

Osmium unites with sulphur in the dry way, or when precipitated from the chlorides by hydrosulphuric acid. The sulphurets obviously correspond to the number of the oxides. (Berzelius.)

Iridium.—In the process already described for separating osmium from its ore, oxide of iridium is left in combination with potassa, after the soluble compound of osmium has been removed by the action of water. On digesting the mass in hydrochloric acid, a blue solution is obtained; but it afterwards becomes of an olive-green hue, and subsequently acquires a deep red tint. This variety of colour, which suggested the name of iridium (Iris, the rainbow), is owing to the successive production of different compounds. In general, after treatment with hydrochloric acid, some undecomposed ore remains, which, from its refractory nature, often requires repeated fusion with nitre.

The chloride of iridium obtained by the foregoing process is distinguished by forming with water a red solution, which is rendered colourless by the pure alkalies or alkaline earths, by hydrosulphuric acid, infusion of gall-nuts, or ferrocyanuret of potassium. It is decomposed by nearly all the metals except gold and platinum, iridium being thrown down in the metallic state. The metal may also be procured by exposing the chloride to a red heat.

Iridium is a brittle metal, and apt to fall into powder when burnished; but with care it may be polished, and then acquires the appearance of platinum. Of all known metals it is the most infusible: Mr. Children, by means of his large galvanic battery, fused it into a globule of a brilliant metallic lustre and white colour, having a density of 18.68; but the attempts at fusion by Berzelius were unsuccessful. Its greatest specific gravity in the unfused state is 15.8629. It is oxidized at a red heat in the open air, if in a state of fine division, but not otherwise; and it is attacked with difficulty even by nitro-hydrochloric acid.

The equivalent of iridium is estimated by Berzelius at 98.8, being identical with that of platinum. It forms with oxygen four oxides exactly analogous in composition to the four first oxides of osmium in the foregoing table, and its four chlorides correspond to those of osmium. Its sulphurets have been little examined, but they doubtless correspond to the oxides. (An. de Ch. et de Ph. xl. 257, and xlii. 185.)

Oxides of Iridium.—The protoxide, sesquioxide, and teroxide are precipitated by alkalies from the chloride to which each is respectively proportional. The *protoxide* is greenish-gray as a hydrate, and black when anhydrous. The *sesquioxide* is bluish-black in the dry state, and deep brown as a hydrate. The hydrated *teroxide* is of a yellowish-brown or greenish colour. The *binoxide* has not hitherto been insulated. Berzelius has not fully decided the nature of the compound which is considered as the blue oxide, that which forms a blue solution with acids; but he believes it to be a compound of the protoxide and sesquioxide. This variety of oxides, together with the facility with which they appear to pass from one to the other, amply accounts for the diversity of tints sometimes observed in solutions of iridium.

Chlorides of Iridium.—The *protochloride* is obtained as a light powder of a deep olive-green colour, by transmitting chlorine gas over pulverulent iridium heated to a commencing red heat. When heated to redness its chlorine is expelled. It is insoluble in water, and but sparingly dissolved by acids, even the nitro-hydrochloric; but when the hydrated protoxide is digested in the hydrochloric acid, the protochloride is reproduced and dissolved, forming probably a soluble compound of the protochloride and hydrochloric acid. Its solution is a mixture of brown, green, and yellow. (Berzelius.)

The *sesquichloride* is best obtained by calcining iridium with nitre, digesting the product in nitric acid, and, after washing, dissolving the residual oxide in hydrochloric acid. Its solution has a dark yellowish-brown tint, which is so intense that a small quantity renders water opaque. By evaporation it yields a black mass, wholly uncrystalline, and deliquescent in the air.

The *bichloride* is formed by digesting at a moderate heat the sesquichloride in nitro-hydrochloric acid. It is deliquescent and very soluble, yielding a solution of a dark reddish-brown colour. When its solution is evaporated to dryness, except at a heat not exceeding 104°, it loses chlorine, and is reconverted into the sesquichloride.

The *terchloride* has not been obtained in a separate form, but only as a double chloride with potassium. It appears to be the principal compound formed in the process above given for extracting iridium from its ore, and is recognized by its rose-red tint.

Iridium has a considerable affinity for carbon, combining with it when a piece of metal is held in the flame of a spirit-lamp. The resulting carburet contains 19.8 per cent. of carbon.

SECTION XXIX.

METALLIC COMBINATIONS.

Having completed the history of the individual metals, and of the compounds resulting from their union with the simple non-metallic bodies, I shall treat briefly in the present section of the combinations of the metals with each other. These compounds are called *alloys*; and to those alloys, of which mercury is a constituent, the term *amalgam* is applied. It is probable that each metal is capable of uniting in one or more proportions with every other metal, and on this supposition the number of alloys would be exceedingly numerous. This department of chemistry, however, owing to its having been cultivated with less zeal than most other branches of the science, is as yet limited, and our knowledge concerning it imperfect. On this account I shall mention those alloys only to which some particular interest is attached.

Metals do not combine with each other in their solid state, owing to the influence of chemical affinity being counteracted by the force of cohesion. It is necessary to liquefy at least one of them, in which case they always unite, provided their mutual attraction is energetic. Thus, brass is formed when pieces of copper are put into melted zinc; and gold unites with mercury at common temperatures by mere contact.

Metals appear to unite with one another in every proportion, precisely in the same manner as sulphuric acid and water. Thus there is no limit to the number of alloys of gold and copper. It is certain, however, that metals have a tendency to combine in definite proportion; for several atomic compounds of this kind occur native. The crystallized amalgam of silver, for example, is composed, according to the analysis of Klaproth, of 64 parts of mercury and 36 of silver, numbers which are so nearly in the ratio of 202 to 108, that the amalgam may be inferred to contain one equivalent of each of its elements. It is indeed possible that the variety of proportion in alloys is rather apparent than real, arising from the mixture of a few definite compounds with each other, or with uncombined metal; an opinion not only suggested by the mode in which alloys are prepared, but in some measure supported by observation. Thus, on adding successive small quantities of silver to mercury, a great variety of fluid amalgams are apparently produced; but, in reality, the chief, if not the sole compound, is a solid amalgam, which is merely diffused throughout the fluid mass, and may be separated by pressing the liquid mercury through a piece of thick leather.

This view is strengthened by some late experiments by Rudberg. (An. de Ch. et de Ph. xlviii. 363.) He finds that variable mixtures of metals in cooling after fusion, have generally two periods when the thermometer is stationary. In alloys of lead and tin one of these points is uniformly at 368½° for all mixtures, while the other point varies according as one or the other metal is predominant, and is near the fusing point of the predominating metal. From this it is inferred that the latter point is caused by the congelation of the predominating metal, and the constant point is the congealing temperature of an alloy of uniform composition present in all the mixtures. This alloy is composed of three equivalents of tin and one eq. of lead, its congealing point being 368½°. In variable mixtures of bismuth and tin the constant point is 289½°, which is the congealing temperature of an alloy composed of single equivalents of tin and bismuth.

Alloys are analogous to metals in their chief physical properties. They are opaque, possess the metallic lustre, and are good conductors of heat and electricity. They often differ materially in some respects from the elements of which they consist. The colour of an alloy is sometimes different from that of its constituents, of which brass is a remarkable example. The hardness of a metal is in general increased by being alloyed, and for this reason its elasticity and sonorousness are frequently improved. The malleability and ductility of metals, on the contrary, are usually impaired by combination. Alloys formed of two brittle metals are always brittle; and an alloy composed of a ductile and a brittle metal is generally brittle, especially if the latter predominate. An alloy of two ductile metals is sometimes brittle.

The density of an alloy is sometimes less, sometimes greater, than the mean density of the metals of which it is composed.

The fusibility of metals is greatly increased by being alloyed. Thus pure platinum, which cannot be completely fused in the most intense heat of a wind furnace, forms a very fusible alloy with arsenic.

The tendency of metals to unite with oxygen is considerably augmented by being alloyed. This effect is particularly conspicuous when dense metals are liquefied by combination with quicksilver. Lead and tin, for instance, when united with mercury, are soon oxidised by exposure to the atmosphere; and even gold and silver combine with oxygen, when the amalgams of those metals are agitated with air. The oxidability of one metal in an alloy appears in some instances to be increased in consequence of a galvanic action. Thus, Faraday observed, that an alloy of steel with 100th of its weight of platinum was dissolved with effervescence in dilute sulphuric acid, which was so weak that it scarcely acted on common steel; an effect which he ascribes to the steel in the alloy being rendered positive by the presence of the platinum. De la Rive has noticed a similar instance in commercial zinc, the oxidability of which is increased by the presence of small quantities of iron. In these cases, however, the effect is due rather to one metal being mechanically enveloped in another than to actual combination.

AMALGAMS.

Quicksilver unites with potassium when agitated in a glass tube with that metal, forming a solid amalgam. When the amalgam is put into water, the potassium is gradually oxidized, hydrogen gas is disengaged, and the mercury resumes its liquid form. A similar compound may be obtained with sodium. These amalgams may also be procured by placing the negative wire in contact with a globule of mercury during the process of decomposing potassa and soda by galvanism.

A solid amalgam of tin is employed in making looking-glasses; and an amalgam made of one part of lead, one of tin, two of bismuth, and four parts of mercury, is used for silvering the inside of hollow glass globes. This amalgam is solid at common temperatures; but it is fused by a slight degree of heat.

The amalgam of zinc and tin, used for promoting the action of the electrical machine, is made by fusing one part of zinc with one of tin, and then agitating the liquid mass with two parts of hot mercury placed in a wooden box. Mercury evinces little disposition to unite with iron, and on this account, it is usually preserved in iron bottles.

The amalgam of silver, as already mentioned, is a mineral production. The process of separating silver from its ores by amalgamation, practised on a large scale at Freyberg in Germany, is founded on the affinity of mercury for silver. On exposing the amalgam to heat, the quicksilver is volatilized, and pure silver remains.

Gold unites with remarkable facility with mercury, forming a white-coloured compound. An amalgam composed of one part of gold and eight of mercury is employed in gilding brass. The brass, after being rubbed with nitrate of oxide of mercury in order to give it a thin film of quicksilver, is covered with the amalgam of gold, and then exposed to heat for the purpose of expelling the mercury.

ALLOYS OF ARSENIC.

Arsenic has a tendency to render the metals with which it is alloyed, both brittle and fusible. It has the property of destroying the colour of gold and copper. An alloy of copper, with a tenth part of arsenic, is so very similar in appearance to silver, that it has been substituted for it. The whiteness of this alloy affords a rough mode of testing for arsenic; for if arsenious acid and charcoal be heated between two plates of copper, a white stain afterwards appears upon its surface, owing to the formation of an arseniuret of copper.

The presence of arsenic in iron has a very pernicious effect; for even though in small proportion, it renders the iron brittle, especially when heated.

The alloy of tin and arsenic is employed for forming arseniuretted hydrogen gas by the action of hydrochloric acid. The tin of commerce sometimes contains a minute quantity of this alloy.

An alloy of platinum with ten parts of arsenic is fusible at a heat a little above redness, and may, therefore, be cast in moulds. On exposing the alloy to a gradually increasing temperature in open vessels, the arsenic is oxidized and expelled, and the platinum recovers its purity and infusibility.

ALLOYS OF TIN, LEAD, ANTIMONY, AND BISMUTH.

Tin and lead unite readily when fused together, constituting solder, of which two kinds are distinguished. The alloy called *fine solder* consists of two parts of tin and one of lead, fuses at about 360°, and is much employed in tinning copper. The *coarse solder* contains 1-4th of tin, fuses at about 500°, and is the substance used for soldering by glaziers. Thus, by varying the relative quantity of the metals, a solder of different fusibility may be obtained. The process of hard soldering or *brazing*, by which two surfaces of copper are cemented together, is done with *hard solder*, which is made by fusing together brass and zinc: the copper requires to be heated, when this solder is used, to near its point of fusion.

It has been observed by Kupfer that most of the *alloys* of tin and lead, made in atomic proportion, have a specific gravity less than their calculated density; from which it is manifest that they expand in uniting. The *amalgams* of lead and tin, on the contrary, occupy less space, when combined, than their elements did previously.

Tin, alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter. Inferior sorts contain a large proportion of lead.

Tin, lead, and bismuth form an alloy which is fused at a temperature below 212°. The best proportion, according to D'Arcet, is 8 parts of bismuth, 5 of lead, and 3 of tin.

An alloy of three parts of lead to one of antimony constitutes the substance of which types for printing are made.

A native alloy of antimony and nickel, found at Andreasberg in the Harz, was found by Stromeyer to consist of 29.5 parts or one eq. of nickel, and 64.6 parts or one eq. of antimony.

ALLOYS OF COPPER.

Copper forms with tin several valuable alloys, which are characterized by their sonorousness. Bronze is an alloy of copper with about eight or ten per cent. of tin, together with small quantities of other metals which are not essential to the compound. Cannons are cast with an alloy of a similar kind.

The best bell-metal is composed of 80 parts of copper and 20 of tin;—the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A specimen of English bell-metal was found by Dr. Thomson to consist of 80 parts of copper, 10.1 of tin, 5.6 of zinc, and 4.3 of lead. Lead and antimony, though in small quantity, have a remarkable effect in diminishing the elasticity and sonorousness of the compound. *Speculum-metal*, with which mirrors for telescopes are made, consists of about two parts of copper and one of tin. The whiteness of the alloy is improved by the addition of a little arsenic.

Copper and zinc unite in several proportions, forming alloys of great importance in the arts. The best brass consists of four parts of copper to one of zinc; and when the latter is in a greater proportion, compounds are generated which are called *tombac*, *Dutch-gold*, and *pinchbeck*. The *white copper* of the Chinese is composed, according to the analysis of Dr. Fyfe, of 40.4 parts of copper, 25.4 of zinc, 31.6 of nickel, and 2.6 of iron.

The art of tinning copper consists in covering that metal with a thin layer of tin, in order to protect its surface from rusting. For this purpose, pieces of tin are placed upon a well polished sheet of copper, which is heated sufficiently for fusing the tin. As soon as the tin liquefies, it is rubbed over the whole sheet of copper, and, if the process is skilfully conducted, adheres uniformly to its surface. The oxidation of the tin, a circumstance which would entirely prevent the success of the operation, is avoided by employing fragments of resin or muriate of ammonia, and regulating the temperature with great care. The two metals do not actually combine; but the adhesion is certainly owing to their mutual affinity. Iron, which has a weaker attraction than copper for tin, is tinned with more difficulty than that metal.

ALLOYS OF STEEL.

Messrs. Stodart and Faraday have succeeded in making some very important alloys of steel with other metals. (Philos. Trans. for 1822.) Their experiments induced them to believe that the celebrated Indian steel, called *wootz*, is an alloy of steel with small quantities of silicium and aluminium; and they succeeded in preparing a similar compound, possessed of all the properties of wootz. They ascertained that silver combines with steel, forming an alloy, which, although it contains only 1-500th of its weight of silver, is superior to wootz or the best cast steel in hardness. The alloy of steel with 100th part of platinum, though less hard than that with silver, possesses a greater degree of toughness, and is, therefore, highly valuable when tenacity as well as hardness is required. The alloy of steel with *rhodium* even exceeds the two former in hardness. The compound of steel with palladium, and of steel with iridium and osmium, is likewise exceedingly hard; but these alloys cannot be employed extensively, owing to the rarity of the metals of which they are composed.

ALLOYS OF SILVER.

Silver is capable of uniting with most other metals, and suffers greatly in malleability and ductility by their presence. It may contain a large quantity of copper without losing its white colour. The standard silver for coinage contains about 1-13th part of copper, which increases its hardness, and thus renders it more fit for coins and many other purposes.

ALLOYS OF GOLD.

The presence of other metals in gold has a remarkable effect in impairing its malleability and ductility. The metals which possess this property in the greatest degree are bismuth, lead, antimony, and arsenic. Thus, when gold is alloyed with 1-1920th part of its weight of lead, its malleability is surprisingly diminished. A very small portion of copper has an influence over the colour of gold, communicating to it a red tint, which becomes deeper as the quantity of copper increases. Pure gold, being too soft for coinage and many purposes in the arts, is always alloyed either with copper or an alloy of copper and silver, which increases the hardness of the gold without materially affecting its colour or tenacity. Gold coins contain about 1-12th of copper.

Nearly all the gold found in nature is alloyed more or less with silver. In a late elaborate investigation into the constituents of the Uralian ores of gold, G. Rose found one specimen with 0.16 per cent of silver, and another with 38.38 per cent.; but most of the specimens contained 8 or 9 per cent. of silver. It has been maintained that the native alloys of gold and silver are usually in atomic proportion. This statement, however, has been amply disproved by G. Rose: these metals appear to be isomorphous, and hence, like other isomorphous bodies, they crystallize with each other in proportions altogether indefinite. (Pog. Annalen, xxiii. 161.)

SALTS.

GENERAL REMARKS ON SALTS.

The preceding pages contain the description either of elementary principles, or of compounds immediately resulting from the union of those elements. These compounds are chiefly bi-elementary, that is, arise from the union of two elements; and in those which violate the rule, such as hydrocyanic acid and sulphocyanuret of potassium, the bi-elementary character is still conspicuous: hydrocyanic acid does not consist of carbon, nitrogen, and hydrogen, nor sulphocyanuret of potassium of its elements, indiscriminately combined; but the cyanogen and sulphuret of cyanogen assume the functions of elements, and combine as such with the hydrogen and potassium. The affinities of carbon, nitrogen, and sulphur for hydrogen and potassium appear in these combinations to be wholly dormant, and in nowise to contribute to the formation of the sulphocyanuret of potassium and hydrocyanic acid. The constituents of all these compounds are regarded, according to the electro-chemical theory, as possessing opposite electric energies, and as combined by virtue of such energies; and the names applied to them are partly constructed in reference to this theory. Thus in compounds of oxygen and chlorine, chlorine and iodine, sulphur and potassium, the term expressive of the genus or class of bodies to which each compound belongs, is derived from the electro-negative element; so that we do not say chloride of oxygen, iodide of chlorine, and potassiuret of sulphur, but oxide of chlorine, chloride iodine, and of sulphuret of potassium; because oxygen has a higher electro-negative energy than chlorine, chlorine than iodine, and sulphur than potassium. The metals as a class are electro-positive to the non-metallic elements; but in relation to each other some of the metals are electro-positive, and others electro-negative. To the former belong those metals, the oxides of which are strong alkaline bases, such as potassium, sodium, and calcium; and among the latter are enumerated those, such as arsenic, antimony, and molybdenum, which are prone to form acids when they unite with oxygen.

Some of the bi-elementary compounds above referred to, though composed of very energetic elements, are themselves chemically indifferent, manifesting little disposition to unite with any other body whatever; of which the peroxides of manganese and lead, and some of the chlorides are examples. Others, on the contrary, are surprisingly energetic in their chemical relations, and have an extensive range of affinity. The most remarkable instances of this are found among those oxidized bodies called *acids* and *alkalies*, the characters of which fixed the attention of chemists long before their composition was understood. The acids and alkalies, however, are indifferent to elementary substances: their affinities are exerted towards each other, and by uniting they give rise to compounds more complex than themselves, as containing at least three elements, and which are known by the name of *salts*. Acids and alkalies possess opposite electric energies in relation to each other, the former being negative, and the latter positive. The electric energies evinced by them are related to the electric energies of their elements. Thus acids generally abound in the electro-negative oxygen, and if they contain a metal, it is usually an electro-negative metal; whereas the powerful alkalies are the protoxides of electro-positive metals.

Acids and alkalies neutralize each other more or less completely, so that the resulting salt is generally neither acid nor alkaline, and is far less energetic as a chemical agent than acids and alkalies. Most of them, however, unite in definite proportion with certain substances, such as water, alcohol, ammonia, and with other salts, forming the extensive family of *double salts*. To these compounds the electro-chemical theory may be extended: the two simple salts which constitute a double salt, may be viewed as two molecules united by virtue of electric energies of an opposite character.

In the early period of modern chemistry, an acid was considered to be an oxidized body which has a sour taste, reddens litmus paper, and neutralizes alkalies. But subsequent experience has shown the propriety of extending the definition of an acid. For, first, the discovery of the hydracids proved that oxygen is not essential to acidity. Secondly, some compounds, owing to their insolubility, neither taste sour nor redden litmus, and yet from their chemical relations are regarded as acids. Thirdly, some acknowledged acids, such as the carbonic and hydrosulphuric, are unable fully to destroy the alkaline reaction of potassa. Facts of this kind have induced chemists to consider as acids all those compounds which unite with potassa or ammonia, and give rise to bodies similar in their constitution and general character to the salts which the sulphuric or some admitted acid forms with those alkalies.

A similar extension is given to the notion of alkalinity, the characters of which, as exhibited in their most perfect form in potassa and soda, are causticity, a peculiar pungent alkaline taste, alkaline reaction with test paper, and power both of neutralizing acids and of forming with them neutral saline compounds. Of these, chemists agree to consider the last as the most characteristic, and place among the *alkaline or salifiable bases* all those bodies which unite definitely with admitted acids, such as the sulphuric and nitric, and form with them compounds analogous in constitution to the salts which admitted alkalies form with the acids. Thus, magnesia is a very strong alkaline base, seeing that 20.7 parts of it neutralize as much sulphuric acid as 47.15 of potassa; and yet magnesia, from being insoluble, is all but tasteless, and has barely any alkaline reaction.

The progress of chemistry, which has gradually developed sounder views of the nature of acids and alkalies, is also causing an extension in the idea of a salt. The great mass of the salts are compounds of oxidized bodies, both the acid and the base containing oxygen. But ammonia, though not an oxide, has all the characters of alkalinity in an eminent degree, and its compounds with acids were at once admitted into the list of salts. Then came the discovery of the hydracids, such as the hydrochloric and hydriodic, which are so powerfully acid, that their compounds with alkaline bases were readily adopted as salts. Hence arose the division of the salts as a class into two orders, one containing oxygen or oxy-salts and the other hydrogen or hydro-salts. Again, the gaseous terfluoride of boron, which contains neither oxygen nor hydrogen, combines definitely with ammonia, and forms with it a neutral compound, which was esteemed a salt as soon as it was known.

The notion of a salt has of late been still further extended. Chemists have long known that metallic sulphurets occasionally combine together, and constitute what is called a *double sulphuret*. In these compounds Berzelius, whose labours have greatly added to their number, has traced an exact analogy with the salts, and applied to them the name of *sulphur-salts*. The simple sulphurets, by the union of which a sulphur-salt is formed, are bi-elementary compounds, strictly analogous in their constitution to acids and alkaline bases, and which like them are capable of assuming opposite electric energies in relation to each other. Electro-positive sulphurets, termed *sulphur-bases*, are usually the protosulphurets of electro-positive metals, and, therefore, correspond to the alkaline bases of those metals; and the electro-negative sulphurets, *sulphur-acids*, are the sulphurets of electro-negative metals, and are proportional in composition to the acids which the same metals form with oxygen. Hence, if the sulphur of a sulphur-salt were replaced by an equivalent quantity of oxygen, an oxy-salt would result. (An. de Ch. et de Ph. xxxii. 60.)

The compounds which Berzelius has enumerated as sulphur-acids, are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold. To these he has added the sulphurets of several other substances not metallic, such as sulphuret of selenium, bisulphuret of carbon, and the hydrosulphuric and hydrosulphocyanic acids. He mentions, also, that just as two electro-positive oxides may combine, one becoming electro-negative in regard to the other, so may a sulphur-salt be generated by the union of electro-positive sulphurets. The native double sulphuret of copper and iron, and a considerable number of similar compounds are instances of this nature. These analogies are rendered much closer by the facts that hydrosulphuric and hydrosulphocyanic acids act as hydracids with ammonia, and as sulphur-acids with sulphur bases, and that all the sulphurets which are remarkable as *sulphur-acids* have likewise the property of combining with ammonia. I shall accordingly place the double sulphurets as a third order of the class of salts, and describe them under the name of sulphur-salts.

A fourth order of salts has been formed by Berzelius, comprising for the most part bi-elementary compounds, which consist of a metal on the one hand, and of chlorine, iodine, bromine, fluorine, and the radicals of the hydracids on the other. He has applied to them the name of *haloid-salts* (from ἁλς sea-salt, and εἶδος form), because in constitution they are analogous to sea-salt The whole series of the metallic chlorides, iodides, bromides, and fluorides, such as chloride of sodium, iodide of potassium, and fluor spar, as well as the cyanurets, sulphocyanurets, and ferrocyanurets, are included in his list of haloid-salts. (An. de Ch. et de Ph. xxxii. 60.) The reader will at once perceive that these haloid-salts, as bi-elementary compounds, differ in composition from other salts, and are analogous to oxides and sulphurets This resemblance will appear still more intimate, if he turn to the tables of composition given in the sections on the metals; where the number and constitution of the chlorides and iodides are shown to be strikingly similar to the number and constitution of the oxides and sulphurets. But Berzelius, though he has himself traced and fully admits these analogies, considers his haloid-salts to differ so much in their chemical relations from oxides and sulphurets, that they ought not to stand in the same class of compounds. Soda, for instance, is caustic, strongly alkaline, and endowed with powerful affinities; while chloride of sodium is a neutral substance, of a taste and appearance precisely like ordinary salts, and indifferent in its chemical relations. The difference is here certainly very striking; but on extending the comparison to other oxides and chlorides, the result is by no means the same. Surely the terchloride of gold is at least as energetic an agent as the peroxide, and the bichloride of platinum as the corresponding oxide. The bichloride and bicyanuret of mercury are more energetic as chemical agents than bisulphuret of mercury, and perhaps fully as much so as the binoxide. Chemists are only beginning to be acquainted with the numerous compounds which metallic cyanurets are capable of forming with each other.

If the difference between all oxides and chlorides were as strong as between soda and sea-salt, chemists would have to consider whether they should adopt as a principle of classification analogy of composition or of character. But as the case now stands they are scarcely left to this alternative. In point of composition the chlorides are as remote from salts as they are allied to oxides; and in their chemical agencies, the haloid-salts of Berzelius, taken collectively, appear to me to be as closely related to oxides and sulphurets as to salts. It seems then fair to conclude that the chlorides and similar bi-elementary compounds stand to each other in the relation of acids and bases, being capable of assuming opposite electric energies, and of forming compounds analogous to salts. I shall describe them as a fourth order of salts under the name of haloid-salts; because the electro-positive and electro-negative compounds which form them, *the haloid bases and acids* have the *same kind of composition as sea-salt.* The haloid-salts of Berzelius are my haloid acids and bases, and what I term a haloid-salt is a double haloid-salt to Berzelius. The doctrine here adopted was first proposed and ably illustrated by Bonsdorff.* (An. de Ch. et de Ph. xliv. 189.)

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* This same doctrine was proposed and ably supported by Dr. Hare, in a

Consistently with the views developed in the preceding pages, I have grouped together all saline compounds which have a certain similarity of composition into one great class of *salts*, which is divided into the four following orders:—

Order I. The oxy-salts. This order includes no salt the acid or base of which is not an oxidized body.

Order II. The hydro-salts. This order includes no salt the acid or base of which does not contain hydrogen.

Order III. The sulphur-salts. This order includes no salt the electro-positive or negative ingredient of which is not a sulphuret.

Order IV. The haloid-salts. This order includes no salt the electro-positive or negative ingredient of which is not haloidal.

The nomenclature of the first order of salts was explained on a former occasion (page 123). The insufficiency of the division into *neutral*, *super*, and *sub*-salts will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name. Secondly, some salts have an acid reaction, and might, therefore, be denominated super-salts, although they do not contain an excess of acid. Nitrate of oxide of lead, for instance, has the property of reddening litmus paper; whereas it consists of one equivalent of oxide of lead and one equivalent of nitric acid, and, therefore, in composition is precisely analogous to nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner. The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined; and in that case the alkali of the litmus being neutralized, its red colour will necessarily be restored. It is hence apparent that a salt may have an acid reaction without having an excess of acid.

The nomenclature of the hydro-salts is framed on the same principle as that applied to the salts which contain oxygen. With respect to the third and fourth order of salts no general principle of nomenclature has yet been agreed on. Berzelius has extended to them the same nomenclature which he employs for the oxy-salts, and some chemists seem disposed to follow his example; but as new views are apt to be obscured, and their intrinsic value overlooked, by being expressed in new language, I shall confine myself as much as possible to terms with which every chemist is familiar. It is worthy of consideration whether the nomenclature of the sulphur and haloid salts, instead of being purposely assimilated to that of the other salts, should not designedly be kept distinct, in order the more readily to distinguish between analogous compounds.

Nearly all salts are solid at common temperatures, and most of them are capable of crystallizing. The colour of salts is very variable, having no necessary connexion with the colour of their elements. Salts composed of a colourless acid and base are colourless; but a salt, though formed of a coloured oxide or acid, may be colourless; or, if coloured, the tint may differ from that of both of its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the most remarkable one for this property is carbonate of ammonia.

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letter on the Berzelian nomenclature, addressed to Professor Silliman, and dated in June, 1834. Dr. Hare had entertained his peculiar views for some time before the date of his letter, and before he was aware that Bonsdorff had held similar opinions.—*Ed.*

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air, and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on their affinity for water, and on their cohesion: their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect which may be produced by the cohesive power of the salt which has the stronger attraction for water, being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water (An. de Ch. lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will, therefore, require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered rapid by heat, the salt is usually deposited in a confused crystalline mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process is to dissolve a salt in hot water, and when it has become quite cold, to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, and is termed *water of crystallization.* The quantity of combined water is very variable in different saline bodies, but it is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion.* By a strong heat, the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air, a change which is called *efflorescence.* The tendency of salts to undergo this change depends on the dryness and coldness of the air; for a salt which effloresces rapidly in a moderately dry and warm atmosphere, may often be kept without change in one which is damp and cold.

Salts, in crystallizing, frequently enclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation.* Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and oxide of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals and two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the temperature of the air without crystallizing, and may in that state be preserved for months without change. Before removal of the cork, the liquid may often be briskly agitated without losing its fluidity; but on readmitting the air, crystallization commonly commences, and the whole becomes solid in the course of a few seconds. The admission of the air sometimes, indeed, fails in causing the effect; but it may be produced with certainty by agitation or the introduction of a solid body. The theory of this phenomenon is not very apparent. Gay-Lussac has shown that it does not depend on atmospheric pressure (An. de Ch. vol. lxxxvii.); for he finds that the solution may be cooled in open vessels without becoming solid, provided its surface be covered with a film of oil; and I have frequently succeeded in the same experiment without the use of oil, by causing the air of the flask to communicate with the atmosphere by means of a moderately narrow tube. It appears from some experiments of Mr. Graham (Phil. Trans. Edin. 1828), that the influence of the air may be ascribed to its uniting chemically with water; for he has proved that gases which are more freely absorbed than atmospheric air, act more rapidly in producing crystallization. Indeed the rapidity of crystallization, occasioned by the contact of gaseous matter, seems proportional to the degree of its affinity for water.

The same quantity of water may hold several different salts in solution, provided they do not mutually decompose each other. The solvent power of water with respect to one salt is, indeed, sometimes increased by the presence of another, owing to combination taking place between the two salts.

Most salts produce cold during the act of solution, especially when they are dissolved rapidly and in large quantity. The greatest reduction of temperature is occasioned by those which contain water of crystallization.

All the oxy-salts are decomposed by Voltaic electricity, provided they are either moistened or in solution. The acid appears at the positive pole of the battery, and the oxide at its opposite extremity; or if the oxide is of easy reduction, the metal itself goes over to the negative side, and its oxygen accompanies the acid to the positive wire.

The hydro-salts, and doubtless also the sulphur and haloid-salts, are subject to a similar change; but the phenomenon, as respects the two last orders of salts, has been little examined.

CRYSTALLIZATION.

The particles of liquid and gaseous bodies, during the formation of solids, sometimes cohere together in an indiscriminate manner, and give rise to irregular shapeless masses; but more frequently they attach themselves to each other in a certain order, so as to constitute solids possessed of a regularly limited form. The process by which such a body is produced is called *crystallization;* the solid itself is termed a *crystal;* and the science, the object of which is to study the form of crystals, is *crystallography.*

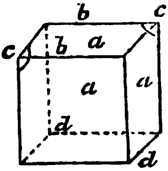
Most bodies crystallize under favourable circumstances. The condition by which the process is peculiarly favoured is the slow and gradual change of a fluid into a solid, the arrangement of the particles being at the same time undisturbed by motion. This is exemplified during the slow cooling of a fused mass of sulphur or bismuth, or the spontaneous evaporation of a saline solution; and the origin of the numerous crystals, which are found in the mineral kingdom, may be ascribed to the influence of the same cause.

Crystallographers have observed that certain crystalline forms are peculiar to certain substances. Thus, calcareous spar crystallizes in rhombohedrons, fluor spar in cubes, and quartz in six-sided pyramids; and these forms are so far peculiar to those substances, that fluor spar never crystallizes in rhombohedrons or six-sided pyramids, nor calcareous spar or quartz in cubes.

Crystalline form may, therefore, serve as a ground of distinction between different substances. It is accordingly employed by mineralogists for distinguishing one mineral species from another; and it is very serviceable to the chemist, as affording a physical character for salts. On this account I have thought it would be useful, before describing the individual salts, to introduce a few pages on crystallization; but from the great extent of the subject, which now constitutes a separate science, my remarks must necessarily be limited, and comprehend little else than an enumeration of the primary forms. To those who are desirous of more ample information, I may recommend Mr. Brooke's "Familiar Introduction to Crystallography," the translation of Mohs's Treatise on Mineralogy by Haidinger, or Mr. Whewell's Essay in the second volume of the Philosophical Transactions of Cambridge.

The surfaces which limit the figure of crystals are called *planes* or *faces*, and are generally flat. The lines formed by the junction of two planes are called *edges*; and the angle formed by two such edges is a *plane angle*. A *solid angle* is the point formed by the meeting of at least three planes. Thus in the cube or hexahedron, fig. 1, *aaa* are planes, *bb* are edges, and *cc* solid angles. The cube it is apparent has six planes or faces, twelve edges, and eight solid angles. Each of the faces has four angles, which are rectangular.

Fig. 1.



The forms of crystals are exceedingly diversified. They are divided by crystallographers into what are called *primitive*, *primary*, *derivative*, *or fundamental* forms, and into *secondary* or *derived* forms. This distinction is founded on the fact, that same substance frequently assumes different crystalline forms; which, however, though actually different, are in general geometrically allied to each other. A body, for instance, whose ordinary figure is a cube, may assume a shape represented by fig. 2, where the general outline is cubic, but the solid angles are replaced by triangular faces; just as if the crystal had been originally a perfect cube, and its eight solid angles subsequently removed. Instead of the solid angles, the edges of the cube may be wanting, and a new form, such as fig. 3, be produced. If the new planes are small, the crystal will preserve its cubic appearance; but if they are larger, the outline of the cube will be less distinct; and should the faces of the original cube wholly disappear, a form altogether different will result. Secondary crystals are those which may be thus deduced by the substitution of planes for the edges or angles of some primary form; and the primary or fundamental form is that from which the former are derived. The replacement is commonly produced by a *tangent plane*, by which, in reference to the edge of a crystal, is meant a plane inclined equally to the two adjacent primary planes and parallel to the edge which it replaces. In allusion to a solid angle, a tangent plane is equally inclined on all the primary planes of which the solid angle is constituted.

Fig. 2.

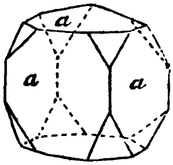
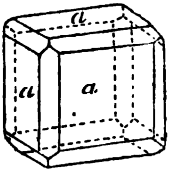


Fig. 3.



The number and kind of primary forms are stated differently by different crystallographers, according to the system which they adopt; but I apprehend it will be most advantageous to the chemical student to be acquainted with those enumerated by Mr. Brooke in the work above mentioned. They are fifteen in number.

1. The first is the hexahedron or cube of geometricians, a figure bounded by six square faces. All the angles of its edges are also equal to 90 degrees. (Fig. 1.)

Fig. 4.

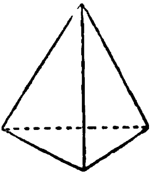
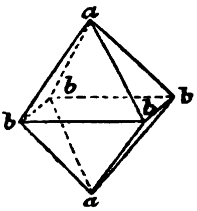


Fig. 5.



2. The tetrahedron, a regular solid of geometry, is contained under four equilateral triangles, and, therefore, all its plane angles are equal to 60 degrees. The faces incline to each other at the edges at an angle of 70° 31′ 44″. (Fig. 4.)

3. The regular octohedron is contained under eight equilateral triangles, fig. 5, and consequently all its plane angles are equal to 60 degrees. The base of the octohedron *bbbb* is a square, and the planes incline on each other at the edges at an angle of 109° 28′ 16″. The octohedron is a regular solid of geometry.

Fig. 6.

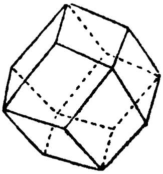
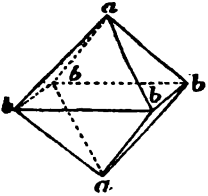


Fig. 7.



4. The rhombic dodecahedron (fig. 6.) is limited by twelve similar rhombic faces, the plane angles of which are equal to 109° 28′ 16″ and 70° 31′ 44″. The faces incline to each other at the edges at an angle of 120°.

5. The octohedron with a square base, fig. 7, is bounded by eight faces which are similar isosceles triangles. The base *bbbb* is always a square, and this is the only part of the figure which is constant.

Fig. 8.

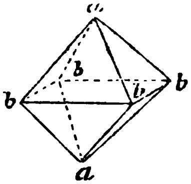
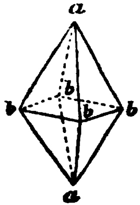


Fig. 9.



6. The rectangular octohedron, fig. 8, is limited by eight isosceles triangles, four of which are different from the other four. The base *bbbb* is always a rectangle; but the ratio of its two sides, as well as all the other dimensions of the figure, is variable.

7. The rhombic octohedron, fig. 9, is contained under eight faces which are similar scalene triangles, and the base *bbbb* is a rhomb. All its dimensions are variable.

Fig. 10.

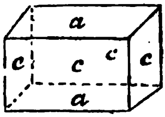
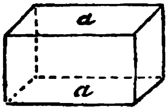


Fig 11.



8. The right square prism, fig. 10, is a six-sided figure, which differs from the cube only in its four *lateral* planes *eccc* being rectangles. The extreme or *terminal* planes *aa* are square. The term *right* denotes that the lateral and terminal planes are inclined to each other at a right angle. It is used in opposition to *oblique*, which signifies that the sides are not perpendicular, but form an oblique angle with the terminal planes.

9. The right rectangular prism, fig. 11, differs from the former in the terminal planes *aa* being rectangular instead of square.

10. **The right rhombic prism**, fig. 12, differs from the two preceding forms only in its terminal planes *aa* being rhombs.

11. The right rhomboidal prism, fig. 13, differs from the preceding form in the terminal planes *aa* being rhomboids.

Fig 12.

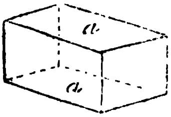
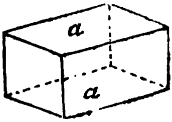


Fig. 13.



12. In the oblique rhombic prism the terminal planes *aa* are rhombic, and the lateral planes form an oblique angle with them. (Fig. 14.)

13. The oblique rhomboidal prism, sometimes called the doubly oblique prism, fig. 15, differs from the preceding form in the terminal planes *aa* being rhomboids.

Fig. 14.

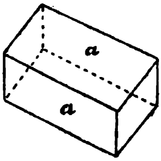
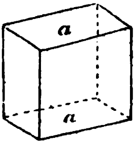


Fig. 15.



14. The rhombohedron, fig. 16, is bounded by six rhombic faces, which are exactly of the same size and form.

Fig. 16.

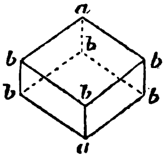
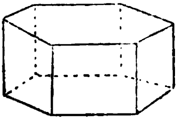


Fig. 17.



15. The regular hexagonal prism, fig. 17, is bounded by six perpendicular or lateral, and two horizontal or terminal planes, which are at right angles to the former. Like the regular hexagon of geometry, the lateral planes incline to each other at an angle of 120 degrees. If these angles are not of 120 degrees, the prism is irregular.

The four first forms are geometrically allied to each other. Thus, if the six solid angles of the regular octohedron are replaced by tangent planes, as in fig. 18, and these are enlarged until they intersect each other, and the faces of the octohedron disappear, a perfect cube is produced. If the twelve edges of the octohedron are replaced by tangent planes, as in figure 19, and these are extended till they mutually intersect, the rhombic dodecahedron will be formed. The cube may by analogous changes be converted into the octohedron, tetrahedron, and rhombic dodecahedron. For if the eight solid angles of the cube be replaced by equilateral triangles, (fig. 2.) and these are enlarged till the planes of the original cube are destroyed, the octohedron results. The tetahedron may be formed by replacing the four solid angles *cc* and *dd* of the cube (fig. 1.) by tangent planes, so that all its original faces disappear. By replacing the twelve edges of the cube with tangent planes as in fig. 3, until the new faces intersect each other, the rhombic dodecahedron will be produced. By the combination of the planes of different primary forms, various secondary ones are created, as is made obvious by the figures, and will be rendered still clearer by making the transitions above described with an apple or potato. The study of such allied forms is very important, because the same substance often occurs in several of these figures, and may assume all of them.

Fig. 18.

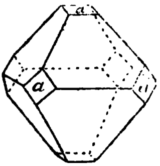
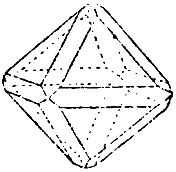


Fig. 19.



The octohedron with a square base is allied to the right square prism. Thus if in fig. 7 two tangent planes are substituted for the solid angles *aa*, and the edges of the base are replaced by faces perpendicular to the former, new forms will result. If the faces of the octohedron disappear, the righsquare prism is formed; but if traces of them remain, secondary forms intermediate between the two primary ones will be produced.

The rectangular and rhombic octohedrons and the right rectangular and rhombic prisms are associated with each other. Thus on replacing the solid angles *aa*, and the four edges of the base of the rectangular octohedron, by tangent planes, and extending them till the planes of the octohedron disappear, the right rectangular prism is formed; and the rhombic octohedron by a similar change is converted into the right rhombic prism. By applying tangent planes to all the edges of the rhombic octohedron except those of the base, the rectangular octohedron may be produced; and by a reversed operation the latter is converted into the former. In this case the solid angles of the rhombic octohedron must be so placed as to bisect the edges of the base of the rectangular octohedron.

The rhombohedron and six-sided or hexagonal prism are allied to each other. If tangent planes are laid on the two solid angles *aa* of the rhombohedron, (fig. 16,) and either the six solid lateral angles marked *b*, or the edges between them, are replaced by equal planes perpendicular to the former, a six-sided prism results; and the six-sided prism may be reconverted into the rhombohedron by replacing all its alternate solid angles by equal and similar rhombic planes.

The six-sided prism is often associated in nature with a double six-sided pyramid, formed by all its terminal edges being replaced by isosceles triangles. If the faces of the prism disappear, the double six-sided pyramid results.

The crystalline forms, which have an intimate geometrical connection with each other, are considered by crystallographers as constituting certain groups, which are termed *Systems of Crystallization*. Thus, of the fifteen primary forms above described, the Tessular System of Mohs comprehends the cube, the tetrahedron, the regular octohedron, and the rhombic dodecahedron, together with several others not enumerated; his Pyramidal System contains the octohedron with a square base, and the right square prism; the Prismatic System contains the rectangular and rhombic octohedron, and the right rectangular and right rhombic prisms; the Hemiprismatic System includes the right rhomboidal and the oblique rhombic prisms; the oblique rhomboidal prism belongs to the Tetarto-prismatic System; and the Rhombohedral System comprehends the rhombohedron and the regular hexagonal prism. This distinction is so far important, that all the forms which a salt or any substance assumes, almost always belong to the same system of crystallization.

Besides the distinction arising from external form, minerals are further distinguished by differences in the mechanical connexion of their particles, peculiarities which mineralogists designate by the name of *structure*. The structure of a mineral arises from its particles adhering at some parts less tenaciously than at others, and consequently yielding to force in one direction more readily than at another. Structure is sometimes visible by holding a mineral between the eye and the light; but in general it is brought into view by effecting the actual separation of parts by mechanical means.

The structure of minerals may be *regular* or *irregular*. It is regular when the separation takes place in such a manner, that the detached surfaces are smooth and even like the planes of a crystal; and it is irregular, when the new surface does not possess this character.

A mineral which possesses a regular structure is said to be *cleavable* or to admit of *cleavage;* the surfaces exposed by splitting or *cleaving* a mineral are termed the *faces of cleavage;* and the direction in which it may be cleaved is called the *direction of cleavage.* Sometimes a mineral is cleavable only in one direction, and is then said to have a *single* cleavage. Others may be cleaved in two, three, four, or more directions, and are said to have a *double*, *treble*, *fourfold* cleavage, and so on, according to their number.

Minerals that are cleavable in more than two directions may, by the removal of layers parallel to the planes of their cleavage, be often made to assume regular primary forms, though they may originally have possessed a different figure. Calcareous spar, for example, occurs in rhombohedrons of different kinds, in hexagonal prisms, in six-sided pyramids, and in various combinations of these forms; but it has three sets of cleavage, which are so inclined to each other as to constitute a rhombohedron of invariable dimensions, and into that form every crystal of calcareous spar may be reduced. Lead glance possesses a treble cleavage, the planes of which are at right angles to each other; and hence it is always convertible by cleavage into the cube. The cleavages of fluor spar are fourfold, and in a direction parallel to the planes of the regular octohedron, into which form every cube of fluor may be converted.

Cleavage not only affords a useful character for distinguishing minerals, but is frequently employed by mineralogists for detecting the primary forms of crystals. If a mineral occur in two or more of those forms which have been enumerated as primary, that one is usually selected as fundamental which may be produced by cleavage. Thus fluor spar is met with in cubes, in the form of the regular octohedron, and as the rhombic dodecahedron. Of these the cube is by far the most frequent; and yet the octohedron is usually adopted as the fundamental form, because fluor has four equally distinct cleavages parallel to the planes of that figure. It is, indeed, a practice very common among mineralogists, not only to consider cleavage as the most influential circumstance in fixing the primary form of a crystal, but to adopt as such no figure which is inconsistent with its cleavages.

Since the forms above enumerated as belonging to the tessular system of crystallization are possessed of fixed invariable dimensions, it is obvious that minerals, or other crystallized bodies included in that system, must often in their primary forms be identical with each other. In the other systems of crystallization this identity is not necessary, because the dimensions of their forms are variable. Thus octohedrons with a square base may be distinguished by the relative length of their axis, some being flat and others acute. Rhombic octohedrons may be distinguished from each other by the relative length of their axis, and the angles of their base. By Hauy it was regarded as an axiom in crystallography, that minerals not belonging to the tessular system are characterized by their form; that though two minerals may in form be analogous, each for instance being a rhombic prism, the dimensions of those prisms are different. Identity of form in crystals not included in the tessular system was thought to indicate identity of composition. But in the year 1819, a discovery, extremely important both to mineralogy and chemistry, was made by Professor Mitscherlich of Berlin, relative to the connexion between the crystalline form and composition of bodies. It appears from his researches,* that certain substances have the property of assuming the same crystalline form, and may be substituted for each other in combination without affecting the external character of the compound. Thus minerals having the crystallization and structure of garnet, and which from their appearance were believed to be such, have been found on analysis to contain different ingredients. Crystals possessed of the form and aspect of alum may be made with sulphates of potassa and peroxide of iron, without a particle of aluminous earth; and a crystal composed of selenic acid and soda will have a perfect resemblance to Glauber's salt. The axiom of Hauy, therefore, requires an essential modification.

To the new branch of science laid open by the discovery of Mitscherlich, the term of *isomorphism* (from ισος equal, and μορφὴ form) is applied: and those substances which assume the same figure are said to be *isomorphous.* Of these isomorphous bodies, several distinct groups have been described by Mitscherlich. One of the most instructive of these includes the salts of arsenic and phosphoric acid. Thus, the neutral phosphate and biphosphate of soda have exactly the same form as the arseniate and binarseniate of soda; phosphate and biphosphate of ammonia correspond to arseniate and binarseniate of ammonia, and the biphosphate and binarseniate of potassa have the same form. Each arseniate has a corresponding phosphate, possessed of the same form possessing the same number of equivalents of acid, alkali, and water of crystallization, and differing in fact in nothing, except that one series contains arsenic and the other an equivalent quantity of phosphorus. A second remarkable group contains the salts of sulphuric, selenic, chromic, and manganic acids. The salts of baryta, strontia, and oxide of lead constitute a third group; and a fourth consists of lime, magnesia, and the protoxides of manganese, iron, cobalt, nickel, zinc, and copper. A fifth includes alumina, peroxide of iron, and the green oxide of chromium; and a sixth group includes the salts of permanganic and perchloric acids. In comparing together isomorphous bodies of the same group, identity of form is not to be expected unless there is similarity of composition. A neutral phosphate does not correspond to a binarseniate, nor a biphosphate to a neutral arseniate: an anhydrous sulphate is not comparable to a hydrated seleniate of the same base; nor is sulphate of protoxide of iron, with six equivalents of water, isomorphous with sulphate of protoxide of manganese with five equivalents. In all such instances, if chemical composition differ, crystalline form is also different.

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* Annales de Ch. et de Physique, vol. xiv. 172, xix. 350, and xxiv. 264 and 355.

The following table contains the principal groups of isomorphous substances at present observed by chemists: a more extended one, partly theoretical, has been drawn up by Professor Johnston, of Durham, in his Report on Chemistry to the British Association:—

1.	
Silver	Ag.
Gold	Au.
2.	
Arsenious acid . . . in its unusual form (page 354.)	$\underline{\overset{\cdots}{\text{As}}}$.
Sesquioxide of antimony .	$\underline{\overset{\cdots}{\text{Sb}}}$.
3.	
Alumina	$\underline{\overset{\cdots}{\text{Al}}}$.
Sesquioxide of iron . . .	$\underline{\overset{\cdots}{\text{Fe}}}$.
4.	
Salts of Phosphoric acid . . .	$\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\text{P}}}$.
Arsenic acid	$\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\text{As}}}$.
5.	
Salts of Sulphuric acid	$\overset{\cdots}{\text{S}}$.
Selenic acid . . .	$\overset{\cdots}{\text{Se}}$.
Chromic acid . . .	$\overset{\cdots}{\text{Cr}}$.
Manganic acid . . .	$\overset{\cdots}{\text{Mn}}$.
6.	
Salts of Perchloric acid . . .	$\underline{\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\text{Cl}}}$.
Permanganic acid . . .	$\underline{\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{\text{Mn}}}$.
7.	
Salts of Potassa.	$\dot{\text{K}}$.
Ammonia with 1 eq. of water	$H^3N+\dot{H}$.

8.	
Salts of Soda	$\dot{\text{Na}}$.
Oxide of silver . . .	$\dot{\text{Ag}}$.
9.	
Salts of Baryta	$\dot{\text{Ba}}$.
Strontia	$\dot{\text{Sr}}$.
Lime (in Arragonite) . .	$\dot{\text{Ca}}$.
Protoxide of lead . .	$\dot{\text{Pb}}$.
10.	
Salts of Lime	$\dot{\text{Ca}}$.
Magnesia . . .	$\dot{\text{Mg}}$.
Protoxide of iron . . .	$\dot{\text{Fe}}$.
manganese .	$\dot{\text{Mn}}$.
zinc . .	$\dot{\text{Zn}}$.
nickel . .	$\dot{\text{Ni}}$.
cobalt .	$\dot{\text{Co}}$.
copper . .	$\dot{\text{Cu}}$.
lead (inplumbo-calcite) .	$\underline{\dot{\text{Pb}}}$.
11.	
Salts of Alumina	$\underline{\overset{\cdots}{\text{Al}}}$.
Sesquioxide of iron .	$\underline{\overset{\cdots}{\text{Fe}}}$.
Sesquioxide of chromium .	$\underline{\overset{\cdots}{\text{Cr}}}$.
Sesquioxide of manganese	$\underline{\overset{\cdots}{\text{Mn}}}$.

The facts above mentioned afford indubitable proof that the form of crystals is materially dependent on their atomic constitution; and they at first induced Mitscherlich to suspect that crystalline form is determined solely by the number and arrangement of atoms, quite independently of their nature. Subsequent observation, however, induced him to abandon this view; and his opinion now appears to be, that certain elements, which are themselves isomorphous, when combined in the same manner with the same substance, communicate the same form. Similarly constituted salts of arsenic and phosphoric acids yield crystals of the same figure, because the acids, it is thought, are themselves isomorphous; and as the atomic constitution of these acids is similar, each containing the same number of atoms of oxygen united with the same number of atoms of the other ingredient, it is inferred that phosphorus is isomorphous with arsenic. In like manner it is believed that selenic acid must be isomorphous with sulphuric acid, and selenium with sulphur; and the same identity of form is ascribed to all those oxides above enumerated, the salts of which are isomorphous. The accuracy of this ingenious view has not yet been put to the test of extensive observation, because the crystalline forms of the substances in question are for the most part unknown. But our knowledge, so far as it goes, is favourable; for sesquioxide of iron and alumina, the salts of which possess the same form, are themselves isomorphous. It may hence be inferred as probable, that isomorphous compounds in general arise from isomorphous elements uniting in the same manner with the same substance.

Isomorphous substances have often very close points of resemblance, quite independently of form. Thus, arsenic and phosphorus have the same odour; they both form gaseous compounds with hydrogen: they differ from nearly all other bodies in their mode of combining with oxygen, and yet agree with one another, and their salts are disposed to combine with the same quantity of water of crystallization. A similar analogy subsists between selenium and sulphur, both being fusible, volatile, and combustible in nearly the same degree, forming with hydrogen colourless gases which are similar in odour and in their chemical relations, and giving rise to analogous compounds with oxygen. The characters of sulphuric and selenic acids in particular are very similar; and the salts of these acids are equally allied. Sulphate of soda, for example, has the unusual property of being less soluble in water at 212° than at 100°, and the very same peculiarity is observable in seleniate of soda. The same intimacy of relation exists between baryta and strontia, between lime and magnesia, and between cobalt and nickel.

Isomorphous substances, owing doubtless to the various points of resemblance which have just been traced, crystallize together with great readiness, and are separated from each other with difficulty. Dr. Daubeny has remarked that a weak solution of lime, which in pure water would be instantly indicated by oxalate of ammonia, is very sluggishly affected by that test when much sulphate of magnesia is present; and I find that chloride of manganese cannot be purified from lime by oxalate of ammonia. A mixture of the sulphates of the protoxides of copper and iron yields crystals which have the same quantity of water of crystallization (six equivalents), and the same form as green vitriol, though they may contain a large quantity of copper. The sulphates of the protoxides of zinc and copper, of copper and magnesium, of copper and nickel, of zinc and manganese, and of magnesium and manganese, crystallize together, contain six equivalents of water, and have the same form as green vitriol, without containing a particle of iron. These mixed salts may be crystallized over and over again without the ingredients being separated from each other, just as it is extremely difficult to purify alum from sesquioxide of iron, with which alumina is isomorphous. In these instances the isomorphous salts do not occur in definite proportions: they are not chemically united as double salts, but merely crystallize together.

The same intermixture of isomorphous substances which takes place in artificial salts, is found to occur in minerals, and affords a luminous explanation of the great variety both in the kind and proportion of substances which may coexist in a mineral species, without its external character being

Consistently with the views developed in the preceding pages, I have grouped together all saline compounds which have a certain similarity of composition into one great class of *salts*, which is divided into the four following orders:—

Order I. The oxy-salts. This order includes no salt the acid or base of which is not an oxidized body.

Order II. The hydro-salts. This order includes no salt the acid or base of which does not contain hydrogen.

Order III. The sulphur-salts. This order includes no salt the electro-positive or negative ingredient of which is not a sulphuret.

Order IV. The haloid-salts. This order includes no salt the electro-positive or negative ingredient of which is not haloidal.

The nomenclature of the first order of salts was explained on a former occasion (page 123). The insufficiency of the division into *neutral*, *super*, and *sub*-salts will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name. Secondly, some salts have an acid reaction, and might, therefore, be denominated super-salts, although they do not contain an excess of acid. Nitrate of oxide of lead, for instance, has the property of reddening litmus paper; whereas it consists of one equivalent of oxide of lead and one equivalent of nitric acid, and, therefore, in composition is precisely analogous to nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner. The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined; and in that case the alkali of the litmus being neutralized, its red colour will necessarily be restored. It is hence apparent that a salt may have an acid reaction without having an excess of acid.

The nomenclature of the hydro-salts is framed on the same principle as that applied to the salts which contain oxygen. With respect to the third and fourth order of salts no general principle of nomenclature has yet been agreed on. Berzelius has extended to them the same nomenclature which he employs for the oxy-salts, and some chemists seem disposed to follow his example; but as new views are apt to be obscured, and their intrinsic value overlooked, by being expressed in new language, I shall confine myself as much as possible to terms with which every chemist is familiar. It is worthy of consideration whether the nomenclature of the sulphur and haloid salts, instead of being purposely assimilated to that of the other salts, should not designedly be kept distinct, in order the more readily to distinguish between analogous compounds.

Nearly all salts are solid at common temperatures, and most of them are capable of crystallizing. The colour of salts is very variable, having no necessary connexion with the colour of their elements. Salts composed of a colourless acid and base are colourless; but a salt, though formed of a coloured oxide or acid, may be colourless; or, if coloured, the tint may differ from that of both of its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the most remarkable one for this property is carbonate of ammonia.

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letter on the Berzelian nomenclature, addressed to Professor Silliman, and dated in June, 1834. Dr. Hare had entertained his peculiar views for some time before the date of his letter, and before he was aware that Bonsdorff had held similar opinions.—*Ed.*

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air, and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on their affinity for water, and on their cohesion: their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect which may be produced by the cohesive power of the salt which has the stronger attraction for water, being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water (An. de Ch. lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will, therefore, require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered rapid by heat, the salt is usually deposited in a confused crystalline mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process is to dissolve a salt in hot water, and when it has become quite cold, to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, and is termed *water of crystallization.* The quantity of combined water is very variable in different saline bodies, but it is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion.* By a strong heat, the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air, a change which is called *efflorescence.* The tendency of salts to undergo this change depends on the dryness and coldness of the air; for a salt which effloresces rapidly in a moderately dry and warm atmosphere, may often be kept without change in one which is damp and cold.

Salts, in crystallizing, frequently enclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation.* Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and oxide of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals and two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the

Names.	Base.	Acid.	Equiv.	Formulæ.
Tersulph. alumina .	51.4	1 eq.+120.3	3 eq.=171.7	$\underline{\dddot{Al}}+3\dddot{S}$.
Do. in crystals with	162 or	18 eq. of water .	=333.7	
Sulph. protox. manganese	35.7	1 eq.+ 40.1	1 eq.= 75.8	$\dot{Mn}+\dddot{S}$.
Do. in crystals with	45 or	5 eq. of water .	=120.8	
Sulph. protox. iron .	36	1 eq.+ 40.1	1 eq.= 76.1	$\dot{Fe}+\dddot{S}$.
Do. in crystals with	54 or	6 eq. of water .	=130.1	
Tersulph. sesquiox. iron	80	1 eq.+120.3	3 eq.=200.3	$\underline{\dddot{Fe}}+3\dddot{S}$.
Disulph. sesquiox. iron	160	2 eq.+ 40.1	1 eq.=200.1	$2\underline{\dddot{Fe}}+\dddot{S}$.
Do. as a hydrate with	54 or	6 eq. of water .	=254.1	
Sulph. protox. zinc .	40.3	1 eq.+ 40.1	1 eq.= 80.4	$\dot{Zn}+\dddot{S}$.
Do. in crystals with	63 or	7 eq. of water .	=143.4	
Sulph. protox. nickel .	37.5	1 eq.+ 40.1	1 eq.= 77.6	$\dot{Ni}+\dddot{S}$.
Do. in crystals with	63 or	7 eq. of water .	=140.6	
Sulph. protox. cobalt .	37.5	1 eq.+ 40.1	1 eq.= 77.6	$\dot{Co}+\dddot{S}$.
Do. in crystals with	54 or	6 eq. of water .	=131.6	
Tersulph. sesquiox. chrom.	80	1 eq.+120.3	3 eq.=200.3	$\underline{\dddot{Cr}}+3\dddot{S}$.
Sulph. protox. copper	39.6	1 eq.+ 40.1	1 eq.= 79.7	$\dot{Cu}+\dddot{S}$.
Disulph. protox. copper	79.2	2 eq.+ 40.1	1 eq.=119.3	$2\dot{Cu}+\dddot{S}$.
Sulph. protox. mercury	210	1 eq.+ 40.1	1 eq.=250.1	$\dot{Hg}+\dddot{S}$
Subsulp. perox. mercury	872	4 eq.+120.3	3 eq.=992.3	$4\ddot{Hg}+3\dddot{S}$.
Bisulph. perox. mercury	218	1 eq.+ 80.2	2 eq.=298.2	$\ddot{Hg}+2\dddot{S}$.
Sulph. ox. silver . .	116	1 eq.+ 40.1	1 eq.=156.1	$\dot{Ag}+\dddot{S}$.

DOUBLE SULPHATES.

Names.				Equiv.	Formulæ.
Sulphate of soda and lime	Sulph. soda do. lime	71.4 68.6	1 eq. 1 eq.	=140	$\dot{Na}\dddot{S}+\dot{Ca}\dddot{S}$.
Sulph. of potassa and magnesia	Sulph. potassa do. magnesia	87.25 60.8	1 eq. 1 eq.	=148.05	$\dot{K}\dddot{S}+\dot{Mg}\dddot{S}$.
Do. with 54 or 6 eq. of water . .				=202.05	
Sulph. of ammonia and magnesia	Sulph. ammonia do. magnesia	57.25 60.8	1 eq. 1 eq.	=118.05	$H^3N\dddot{S}+\dot{Mg}\dddot{S}$.
Do. with 63 or 7 eq. of water . .				=181.05	
Sulph. of soda and magnesia	Sulph. soda do. magnesia	71.4 60.8	1 eq. 1 eq.	=132.2	$Na\dddot{S}+\dot{Mg}\dddot{S}$.
Do. with 54 or 6 eq. of water . .				=186.2	

Names.				Equiv.	Formulæ.
Sulph. of potassa and alumina	Sulph. potassa Tersulph. alum.	87.25 171.7	1 eq. 1 eq.	=258.95	$\dot{K}\dddot{S}+\dddot{\underline{Al}}\dddot{S}_3$
Do. with 216 or 24 eq. of water				=474.95	
Sulph. of soda and alumina	Sulph. soda Tersulph. alum.	71.4 171.7	1 eq. 1 eq.	=243.1	$\dot{Na}\dddot{S}+\dddot{\underline{Al}}\dddot{S}_3$
Do. with 234 or 26 eq. of water				=477.1	
Sulph. of ammonia and alumina	Sulph. ammonia Tersulph. alum.	57.25 171.7	1 eq. 1 eq.	=228.95	$H^3N\dddot{S}+\dddot{Al}\dddot{S}_3$
Sulph. of potassa and protox. mang.	Sulph. potassa do. protox. mang.	87.25 75.8	1 eq. 1 eq.	=163.05	$\dot{K}\dddot{S}+\dot{Mn}\dddot{S}.$
Do. with 54 or 6 eq. of water				=217.05	
Sulph. of ammonia and protox. mang.	Sulph. ammonia do. protox. mang.	57.25 75.8	1 eq. 1 eq.	=133.05	$H^3N\dddot{S}+\dot{Mn}\dddot{S}.$
Do. with 63 or 7 eq. of water				=196.05	

The protoxides of iron, zinc, nickel, and cobalt yield with potassa and ammonia double salts exactly agreeing in form and composition with the preceding double salts of magnesia and oxide of manganese.

Sulphate of Potassa.—This salt is easily prepared artificially by neutralizing carbonate of potassa with sulphuric acid; and it is procured abundantly by neutralizing with carbonate of potassa the residue of the operation for preparing nitric acid. (Page 181.) Its taste is saline and bitter. It generally crystallizes in six-sided prisms, bounded by pyramids with six sides; the size of which is said to be much increased by the presence of a little carbonate of potassa. Its primary form, according to Mitscherlich, is a rhombic octohedron, and it is isomorphous with chromate and seleniate of potassa. (Pog. Annalen, xviii. 168.) The crystals contain no water of crystallization, and suffer no change by exposure to the air. They decrepitate when heated, and enter into fusion at a red heat. They require 16 times their weight of water at 60°, and 5 of boiling water for solution.

Bisulphate of potassa is easily formed by exposing the neutral sulphate with half its weight of strong sulphuric acid to a heat just below redness, in a platinum crucible, until acid fumes cease to escape. The primary form of its crystals is a right rhombic prism, but which is in general so flattened as to be tabular. It has a strong sour taste, and reddens litmus paper. It is much more soluble than the neutral sulphate, requiring for solution only twice its weight of water at 60°, and less than an equal weight at 212° F. It is resolved by heat into sulphuric acid and the neutral sulphate.

Mr. Phillips has described a *sesquisulphate*, obtained in the form of acicular crystals like asbestus, from the residue of the process for making nitric acid. The conditions for ensuring its production have not been determined. (Phil. Mag. and Annals, ii. 421.)

Sulphate of Soda.—This compound, commonly called *Glauber's salt*, is occasionally met with on the surface of the earth, and is frequently contained in mineral springs. It may be made by the direct action of sulphuric acid on carbonate of soda, and it is procured in large quantity as a residue in the process for forming hydrochloric acid and chlorine. (Pages 210 and 212.)

Sulphate of soda has a cooling, saline, and bitter taste. It commonly yields four and six-sided prismatic crystals, but its primary form is a rhombic octohedron. Its crystals effloresce rapidly when exposed to the air, losing the whole of their water. When heated they readily undergo the watery fusion. At 32° 100 parts of water dissolve 12 parts of the crystals, 48 parts at 64.5°, 100 parts at 77°, 270 at 89.5°, and 322 at 91.5°. On increasing the heat beyond this point, a portion of the salt is deposited, being less soluble than at 91.5°. (Gay-Lussac.) If a solution saturated at 91.5° is evaporated at a higher temperature, the salt is deposited in opaque anhydrous prisms, the primary form of which is a rhombic octohedron. Its specific gravity in this state is 2.462. (Haidinger.)

Bisulphate of soda may be formed in the same manner as the analogous salt of potassa.

Sulphate of Lithia.—This salt is very soluble in water, fuses by heat more readily than the sulphates of the other alkalies, and crystallizes in flat prisms, which resemble sulphate of soda in appearance, but do not effloresce on exposure to the air. Its taste is saline without being bitter.

Sulphate of Ammonia.—This salt is easily prepared by neutralizing carbonate of ammonia with dilute sulphuric acid; and it is contained in considerable quantity in the soot from coal. It crystallizes in long flattened six-sided prisms. It dissolves in two parts of water at 60°, and in an equal weight of boiling water. In a warm dry air it effloresces and loses half of its water. When sharply heated it fuses, gives off its water of crystallization along with some ammonia, and is then decomposed, yielding nitrogen gas, water, and sulphate of ammonia.

Sulphate of Baryta.—Native sulphate of baryta, commonly called *heavy spar*, occurs abundantly, chiefly massive, but sometimes in anhydrous crystals, the form of which is variable, being sometimes prismatic and sometimes tabular, deducible from a right rhombic prism. Its density is about 4.4. It is easily formed artificially by double decomposition. This salt bears an intense heat without fusing or undergoing any other change, and is one of the most insoluble substances with which chemists are acquainted. It is sparingly dissolved by hot and concentrated sulphuric acid, but is precipitated by the addition of water.

Sulphate of Strontia.—This salt, the *celestine* of mineralogists, is less abundant than heavy spar. It occurs in anhydrous prismatic crystals of peculiar beauty in Sicily, and its primary form is a right rhombic prism. Its density is 3.858. As obtained by the way of double decomposition, it is a white heavy powder, very similar to sulphate of baryta, and requires about 3840 times its weight of boiling water for solution.

Sulphate of Lime.—This salt is easily formed by mixing in solution a salt of lime with any soluble sulphate. It occurs abundantly as a natural production. The mineral called *anhydrite* is anhydrous sulphate of lime; and all the varieties of *gypsum* are composed of the same salt, united with water. The pure crystallized specimens of gypsum are sometimes called *selenite*; and the white compact variety is employed in statuary under the name of *alabaster*. The crystals are generally flattened prisms, the primary form of which is a rhombic prism. The hydrous salt is deprived of its water by a low red heat, and in this state forms plaster of Paris. Its property of becoming hard, when made into a thin paste with water, is owing to the anhydrous sulphate combining chemically with that liquid, and thus depriving it of its fluidity.

Sulphate of lime has hardly any taste. It is considerably more soluble than the sulphate of baryta or strontia, requiring for solution about 500 parts of cold, and 450 of boiling water. Owing to this circumstance, and to its existing so abundantly in the earth, it is frequently contained in spring water, to which it communicates the property called hardness. When freshly precipitated, it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Dr. Thomson states, that it parts with some of its acid when heated to redness

Sulphate of Magnesia.—This sulphate, generally known by the name of *Epsom* salt, is frequently contained in mineral springs. It may be made directly, by neutralizing dilute sulphuric acid with carbonate of magnesia;

but it is procured for the purposes of commerce by the action of dilute sulphuric acid on magnesian limestone, native carbonate of lime and magnesia.

Sulphate of magnesia has a saline, bitter, and nauseous taste. It crystallizes readily in small quadrangular prisms, which effloresce slightly in a dry air. It is obtained also in larger crystals, which are irregular six-sided prisms, terminated by six-sided summits. Its primary form is a right rhombic prism, the angles of which are 90° 30′ and 89° 30′. (Brooke.) Its crystals are soluble in an equal weight of water at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion when heated; and the anhydrous salt is deprived of a portion of its acid at a white heat.

Sulphates of Alumina.—The *tersulphate* is prepared by saturating dilute sulphuric acid with hydrated alumina, and evaporating. It crystallizes with difficulty in thin flexible plates of a pearly lustre, which contain eighteen eq. of water, and require twice their weight of water for solution. Berzelius says it occurs native at Milo, in the Grecian Archipelago. It has an acid reaction.

The hydrated *disulphate* is known to mineralogists under the name of *aluminite*, which occurs at Halle on the river Saal, and at Newhaven in Sussex; and Berzelius says the same compound falls when ammonia is added to a solution of the tersulphate. It is insoluble in water, and by heat is first rendered anhydrous, and then its acid is expelled, leaving pure alumina. The composition given in the table is from an analysis of aluminite from both its localities by Stromeyer.

Sulphate of Protoxide of Manganese.—This salt is best obtained by dissolving pure carbonate of manganese in moderately dilute sulphuric acid, and setting the solution aside to crystallize by spontaneous evaporation. The crystals are transparent, and of a slight rose tint, in taste resembling Glauber's salt, and occur in flat rhombic prisms. It is insoluble in alcohol, but dissolves in twice and a half its weight of cold water. If the heat is gradually applied, it may be increased to redness without expelling any of the acid.

Sulphates of the Oxides of Iron.—*Sulphate of the protoxide*, commonly called *green vitriol*, is formed by the action of dilute sulphuric acid on metallic iron (page 162), or by exposing protosulphuret of iron in fragments to the combined agency of air and moisture. The salt has a strong styptic, inky taste. Though neutral in composition, being composed of one equivalent of each element, it reddens the vegetable blue colours. It is insoluble in alcohol, but soluble in two parts of cold, and in three-fourths of its weight of boiling water. It occurs in right rhombic prisms, which are transparent, and of a pale green tint; but when its water of crystallization is expelled, it is of a dirty white colour. This salt is employed in the manufacture of fuming sulphuric acid. (Page 194.)

The *tersulphate of the sesquioxide* is formed by mixing with a solution of the protosulphate exactly half as much sulphuric acid as that salt contains, and adding to the mixture in a boiling state successive portions of nitric acid until nitrous acid fumes cease to appear. The solution is then evaporated to dryness to expel the excess of nitric acid, and the tersulphate remains as a white salt. After being strongly heated it dissolves slowly in water; but if evaporated at a gentle heat, it is deliquescent, and very soluble in water and alcohol, but insoluble in strong sulphuric acid. At a red heat it gives out all its acid, and sesquioxide of iron is left. Its solution in water has an orange colour, which is yellow when much diluted.

The *disulphate of the sesquioxide* falls as a hydrate of an ochreous colour, when a solution of the protosulphate is kept in an open vessel.

Sulphate of Protoxide of Zinc.—This salt, frequently called *white vitriol*, is the residue of the process for forming hydrogen gas by the action of dilute sulphuric acid on metallic zinc; but it is also made, for the purposes of commerce, by roasting native sulphuret of zinc. It crystallizes by spontaneous evaporation in transparent flattened four-sided prisms, referable to a right rhombic prism, and isomorphous with Epsom salt. The crystals dissolve in two parts and a half of cold, and are still more soluble in boiling water. The taste of this salt is strongly styptic. It reddens vegetable blue colours, though in composition it is a strictly neutral salt.

Sulphate of Protoxide of Nickel.—This salt, like the salts of nickel in general, is of a green colour, and crystallizes from its solution in pure water in right rhombic prisms exactly similar to the primary form of the sulphates of zinc and magnesia. If an excess of sulphuric acid is present, the crystals are square prisms, which, according to Messrs. R. Phillips and Cooper, contain rather less water and more acid than the preceding; though the difference is not so great as to indicate a different atomic constitution. (Annals of Philosophy, xxii. 439. Dr. Thomson says he analyzed both kinds, and found their composition identical. It is soluble in about three times its weight of water at 60° F.

Sulphate of Protoxide of Cobalt.—When protoxide of cobalt is digested in dilute sulphuric acid, a red solution is formed, which by evaporation deposites crystals of the same colour. Mitscherlich has shown that the crystals are identical in composition with sulphate of protoxide of iron; and Mr. Brooke's measurements prove these salts to be isomorphous. (An. of Phil. N. S. vi. 120.) They are insoluble in alcohol, and dissolve in about 24 parts of cold water.

Tersulphate of Sesquioxide of Chromium.—This salt may be formed by saturating dilute sulphuric acid with hydrated sesquioxide of chromium; but it has not been obtained in crystals.

Sulphates of the Oxides of Copper.—Sulphate of the red oxide of copper has not been obtained in a separate state. The sulphate of the black, or protoxide, *blue vitriol*, employed by surgeons as an escharotic and astringent, may be prepared by roasting the native suphuret; but it is more generally made by directly dissolving the protoxide in dilute sulphuric acid, and crystallizing by evaporation. This salt forms regular crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. It is isomorphous with sulphate of protoxide of manganese.

When pure potassa is added to a solution of the sulphate of protoxide of copper in a quantity insufficient for separating the whole of the acid, a pale bluish-green precipitate, the disulphate, is thrown down.

Sulphate of protoxide of copper and ammonia is generated by dropping pure ammonia into a solution of the sulphate, until the sub-salt at first thrown down is nearly all dissolved. It forms a dark blue solution, from which, when concentrated, crystals are deposited by the addition of alcohol. It may be formed also by rubbing briskly in a mortar two parts of crystallized sulphate of protoxide of copper with three parts of carbonate of ammonia, until the mixture acquires a uniform deep blue colour. Carbonic acid gas is disengaged with effervescence during the operation, and the mass becomes moist, owing to the water of the blue vitriol being set free.

This compound, which is the *ammoniaret of copper* of the Pharmacopœia, contains sulphuric acid, protoxide of copper, and ammonia; but its precise nature has not been determined in a satisfactory manner. It parts gradually with ammonia by exposure to the air.

Sulphates of the Oxides of Mercury.—When two parts of mercury are gently heated in three parts of strong sulphuric acid, so as to cause slow effervescence, a sulphate of the protoxide of mercury is generated. But if a strong heat is employed in such a manner as to excite brisk effervescence, and the mixture is brought to dryness, a bisulphate of the peroxide results, both being anhydrous. (Donovan in An. of Phil. xiv.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow sub-salt, formerly called *turpeth mineral*, subsides. This salt is said by Phillips to consist of three equivalents of acid and four of the peroxide. The hot water retains some of the bisulphate in solution, together with free sulphuric acid.

Sulphate of Oxide of Silver.—As this salt is rather sparingly soluble in water, it may be formed by double decomposition from concentrated solutions of nitrate of oxide of silver and sulphate of soda. It may also be procured by dissolving silver in sulphuric acid which contains about a tenth part of nitric acid, or by boiling silver in an equal weight of concentrated sulphuric acid. It requires about 80 times its weight of hot water for solution, and the greater part is deposited in small needles on cooling. By slow evaporation from a solution containing a little nitric acid, Mitscherlich obtained it in the form of a rhombic octohedron, the angles of which are almost identical with those of anhydrous sulphate of soda. Seleniate of oxide of silver is isomorphous with the sulphate.

Sulphate of oxide of silver forms with ammonia a double salt, which crystallizes in rectangular prisms, the solid angles and lateral edges of which are commonly replaced by tangent planes. It consists of one equivalent of oxide of silver, one of acid, and two of ammonia; and it is formed by dissolving sulphate of oxide of silver in a hot concentrated solution of ammonia, from which on cooling the crystals are deposited. This salt is isomorphous with a double chromate and seleniate of oxide of silver and ammonia, which have a similar constitution, and are formed in the same manner. (Mitscherlich in An. de Ch. et de Ph. xxxviii. 62.)

DOUBLE SULPHATES.

Sulphate of Soda and Lime.—This compound, the Glauberite of mineralogists, occurs in very flat oblique rhombic prisms. Berthier prepared it by fusing together sulphate of soda with sulphate of lime in the ratio of their equivalents. Sulphate of soda, fused in similar proportions with the sulphates of magnesia, baryta, and oxide of lead, gives analogous compounds. In these instances, however, the affinity is so feeble, that it is overcome by the mere action of water. (An. de Ch. et de Ph. xxxviii. 255.)

Sulphate of Potassa and Magnesia.—On mixing solutions of these salts in atomic proportion, the double salt is formed either by spontaneous evaporation or on cooling from a hot rather concentrated solution. The crystals are prismatic, but of a complicated form, derived from an oblique rhombic prism. (Brooke.) A similar double salt, isomorphous with the preceding, is formed by substituting ammonia for potassa. Their composition is given in the table (page 436).

Similar pairs of double salts may be formed with the protoxides of manganese, iron, zinc, cobalt, and nickel. These salts have the same form and composition as the corresponding salt of magnesia.

Alum.—This well known substance is a double sulphate of potassa and alumina, which crystallizes with great facility from a solution containing its elements. It is prepared in this country from alum-slate, an argillaceous slaty rock highly charged with pyrites: on roasting this rock the sulphuret of iron is oxidized, the resulting sulphuric acid unites with alumina and potassa present in the slate, and the alum is dissolved out by water. By frequent crystallization it is purified from the oxide of iron, which obstinately adheres to it. In Italy it is prepared from *alum-stone*, which occurs at Tolfà near Rome, and in most volcanic districts, being formed apparently by the action of sulphurous acid vapours on felspatic rocks. The materials of the alum exist in the stone ready formed; and they are extracted by gently heating the rock, exposing it for a time to the air, and lixiviation. The alum from this source has been long prized, in consequence of being quite free from iron. In both of these processes the alkali contained in the alum-rock is inadequate for uniting with the sulphate of alumina which is obtained, and hence a salt of potassa must be added.

Alum has a sweetish astringent taste, and reddens litmus paper. It is soluble in five parts of water at 60°* and in little more than its own weight

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* The solubility of alum in cold water is probably not so great as is here mentioned. Berzelius states it to be soluble in about eighteen parts of col water, and Thenard in between fourteen and fifteen parts.—*Ed.*

of boiling water. It crystallizes readily in octohedrons, or in segments of the octohedron, and the crystals contain almost 50 per cent. of water of crystallization. On being exposed to heat, they froth up remarkably, and part with all the water, forming anhydrous alum, the *Alumen Ustum* of the Pharmacopœia. At a full red heat the alumina is deprived of its acid.

Alum is employed in the formation of a spontaneously inflammable mixture long known under the name of *Homberg's pyrophorus.* It is made by mixing equal weights of alum and brown sugar, and stirring the mass over the fire in an iron or other convenient vessel till quite dry: it is then put into a glass tube or bottle, and heated to moderate redness without exposure to the air, until inflammable gas ceases to be evolved. A more convenient mixture is made with three parts of lampblack, four of burned alum, and eight of carbonate of potassa. When the pyrophorus is well made, it speedily becomes hot on exposure to the air, takes fire, and burns like tinder; but the experiment frequently fails from the difficulty of regulating the temperature.

From some recent experiments by Gay-Lussac, it appears that the essential ingredient of Homberg's pyrophorus is sulphuret of potassium in a state of minute division. The charcoal and alumina act only by being mechanically interposed between its particles; but when the mass once kindles, the charcoal takes fire and continues the combustion. He finds that an excellent pyrophorus is made by mixing 27 parts of sulphate of potassa with 15 parts of calcined lampblack, and heating the mixture to redness in a common Hessian crucible, of course excluding the air at the same time. (An. de Ch. et de Ph. xxxvii. 415.)

Alum, having exactly the same form, composition, appearance, and taste as the salt just described, may be made with ammonia, the sulphate of which replaces sulphate of potassa. It is met with occasionally as a natural product, and may be prepared by evaporating a solution of sulphate of ammonia with tersulphate of alumina.

A soda alum may also be prepared, similar in form and composition to the preceding alums, except that it contains twenty-six equivalents of water. (Berzelius.) This salt is disposed to effloresce in the air.

Iron Alum.—By mixing sulphate of potassa with tersulphate of sesquioxide of iron, and crystallizing by spontaneous evaporation, crystals are obtained similar to common alum in form, *colour*, *taste*, and composition. This salt has often a pink tint, but is sometimes quite colourless. A similar double salt, quite colourless, may be made with ammonia instead of potassa. In both these alums the alumina is simply replaced by an equivalent quantity of peroxide of iron.

Chrome Alums.—The tersulphate of sesquioxide of chromium forms with the sulphates of potassa and ammonia double salts which are exactly similar in form and composition to the preceding varieties of alum. They appear black by reflected, but ruby-red by transmitted light.

Manganese Alum.—Mitscherlich obtained this salt by mixing a solution of tersulphate of sesquioxide of manganese with sulphate of potassa, and evaporating to the consistence of syrup by a very gentle heat. On cooling, octohedral crystals of a brownish-violet colour were deposited, which were similar in composition to common alum. The tersulphate used for the purpose is prepared by macerating sesquioxide of manganese in very fine powder with strong sulphuric acid: it is made with difficulty, owing to the indisposition of that oxide to unite with acids, and to its ready conversion by heat into sulphate of the protoxide.

Anhydrous Sulphates with Ammonia.—Rose has observed that some sulphates possess the property of absorbing ammonia, and of forming with it definite compounds, which differ from sulphates of ammonia prepared in the moist way, both by containing no water of crystallization, and by the facility with which the alkali is again given out. They are formed by placing the anhydrous sulphate in a glass tube, and transmitting over it at common temperatures ammoniacal gas, well dried by fused potassa, as long as any increase of weight is observed: some sulphates absorb the gas very rapidly at first, and with disengagement of heat; but the absorption afterwards becomes slow, and requires a day or two in order to be complete. The salts most remarkable for this property are those which, in solution, are disposed to unite with ammonia.—Sulphate of protoxide of copper greedily absorbs ammonia, and acquires a deep blue colour similar to the ammoniaret of copper, prepared with moisture; but the former compound consists of two eq. of sulphate of protoxide of copper and five eq. of ammonia, while the latter contains one eq. of sulphate of copper, two of ammonia, and one equivalent of water. Sulphate of protoxide of cobalt, as well as that of nickel, unites with three equivalents of ammonia; that of zinc with 2.5, and that of manganese with two equivalents. The latter when heated loses all its ammonia, and returns to its original condition; whereas most of the other ammoniaco-sulphates suffer partial decomposition at the same time. Sulphate of oxide of silver unites with one equivalent of ammonia; and a similar compound was prepared by C. G. Mitscherlich, but with two equivalents of ammonia. With most of the other anhydrous sulphates ammonia refuses to unite.

On considering the nature of these compounds, one is at first disposed to associate them with double salts, supposing the acid to be divided between the two bases. But this opinion is rendered unlikely by the large quantity of combined ammonia, by the facility with which the alkali is given off, and by the absence of water, so constantly present in other ammoniacal sulphates. Rose, with much plausibility, compares these compounds to hydrates: water acts as a feeble base to saline compounds, combining with some in one or more proportions, and not at all with others, differing greatly in the ratio in which it combines with different salts, and being abandoned with great facility, often by mere exposure to the air. The same features characterize the combinations of ammonia with the anhydrous sulphates. (Pog. Annalen, xx. 149.)

The sulphates are not the only salts which absorb ammonia. Rose found that the nitrate of oxide of silver unites with three equivalents of ammonia, and the gas, if freely supplied, is at first absorbed with such rapidity, and the corresponding increase of temperature is so great, that the salt enters into fusion. Heat expels the ammonia before the nitrate of oxide of silver is decomposed. A similar compound, but with less ammonia, was formed by C. Mitscherlich.

SULPHITES.

The salts of sulphurous acid have not hitherto been minutely examined. The sulphites of potassa, soda, and ammonia, which are made by neutralizing those alkalies with sulphurous acid, are soluble in water, but most of the other sulphites, so far as is known, are of sparing solubility. The sulphites of baryta, strontia, and lime are very insoluble; and consequently the soluble salts of these earths decompose the alkaline sulphites.

The stronger acids, such as the sulphuric, hydrochloric, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognized by its odour. Nitric acid, by yielding oxygen, converts the sulphites into sulphates.

When the sulphites of the fixed alkalies and alkaline earths are strongly heated in close vessels, a sulphate is generated, and a portion of sulphur sublimed. In open vessels at a high temperature they absorb oxygen, and are converted into sulphates; and a similar change takes place even in the cold, especially when they are in solution. Gay-Lussac has remarked, that a neutral sulphite always forms a neutral sulphate when its acid is oxidized; a fact from which it may be inferred, that neutral sulphites consist of one equivalent of the acid and one equivalent of the base.

The hyposulphates and hyposulphites are of such little practical importance, that it is unnecessary to describe individual salts: their general character has been already given. (Page 197.) For a particular description of the hyposulphates, the reader is referred to an essay by Dr. Heeren. (An. de Ch. et de Ph. xl. 30.)

NITRATES.

The nitrates may be prepared by the action of nitric acid on metals, on the salifiable bases themselves, or on carbonates. As nitric acid forms soluble salts with all alkaline bases, the acid of the nitrates cannot be precipitated by any reagent. They are readily distinguished from other salts, however, by the characters already described. (Page 184.)

All the nitrates are decomposed without exception by a high temperature; but the changes which ensue are modified by the nature of the oxide. Nitrate of oxide of palladium is decomposed at such a moderate temperature, that a great part of the acid passes off unchanged. Nitrate of oxide of lead requires a red heat, by which it is resolved, as already mentioned (page 180), into oxygen and nitrous acid. In some instances the changes are more complicated. With nitre, for example, nitrite of potassa is at first generated, with escape of oxygen gas: as the heat increases, the nitrous acid is resolved into binoxide of nitrogen and oxygen, the former of which remains in combination with potassa; the binoxide is then resolved into protoxide of nitrogen and oxygen, the former being retained by the alkali; and, *lastly*, nitrogen gas is disengaged, and peroxide of potassium remains. If the operation is performed in an earthen vessel, the peroxide will be more or less decomposed, in consequence of the affinity of the earthy substances for potassa. The preceding facts have been chiefly collected from the observations of Phillips and Berzelius. The tendency of potassa and soda to unite with protoxide of nitrogen was first observed by Davy; and M. Hess has lately remarked that similar compounds are obtained with soda, baryta, and lime, as well as potassa, when their nitrates are heated, until the disengaged gas is found to extinguish a light.

As the nitrates are easily decomposed by heat alone, they must necessarily suffer decomposition by the united agency of heat and combustible matter. The nitrates on this account are much employed as oxidizing agents, and frequently act with greater efficacy even than nitro-hydrochloric acid. Thus metallic titanium, which resists the action of these acids, combines with oxygen when heated with nitre. The efficiency of this salt, which is the nitrate usually employed for the purpose, depends not only on the affinity of the combustible for oxygen, but likewise on that of the oxidized body for potassa. The process for oxidizing substances by means of nitre is called *deflagration*, and is generally performed by mixing the inflammable body with an equal weight of the nitrate, and projecting the mixture in small portions at a time into a red-hot crucible.

All the neutral nitrates of the fixed alkalies and alkaline earths, together with most of the neutral nitrates of the common metals, are composed of one equivalent of nitric acid, and one equivalent of a protoxide. Consequently, the oxygen of the oxide and acid in all such salts must be in the ratio of 1 to 5, the general formula being $\dot{M}+\overset{\cdot\cdot\cdot\cdot\cdot}{N}$

The only nitrates found native are those of potassa, soda, lime, and magnesia.

The composition of the principal nitrates is exhibited in the following table.—

Names.	Base.	Acid.	Equiv.	Formulæ.
Nitrate of potassa . .	47.15 1 eq.	+ 54.15 1 eq.	= 101.3	$\dot{K}+\overset{\cdot\cdot\cdot\cdot\cdot}{N}$.
———— soda . .	31.3 1 eq.	+ 54.15 1 eq.	= 85.45	$\dot{Na}+\overset{\cdot\cdot\cdot\cdot\cdot}{N}$.
———— ammonia .	17.15 1 eq.	+ 54.15 1 eq.	= 71.3	$H^3N+\overset{\cdot\cdot\cdot\cdot\cdot}{N}$.
Do in prisms with 9 or 1 eq. of water . .			= 80.3	

Names.	Base.	Acid.	Equiv.	Formulæ.
Nitrate of baryta . .	76.7 1 eq.	+54.15 1 eq.	=130.85	$\overset{\cdot}{\mathrm{Ba}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
——— strontia . .	51.8 1 eq.	+54·15 1 eq.	=105.95	$\overset{\cdot}{\mathrm{Sr}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Do. in prisms with 45 or 5 eq. of water . .			=150·95	
Nitrate of lime . .	28.5 1 eq.	+54.15 1 eq.	= 82.65	$\overset{\cdot}{\mathrm{Ca}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
——— magnesia .	20.7 1 eq.	+54.15 1 eq.	= 74.85	$\overset{\cdot}{\mathrm{Mg}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
——— protox. copper	39.6 1 eq.	+54.15 1 eq.	= 93.75	$\overset{\cdot}{\mathrm{Cu}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Do. in prisms with 63 or 7 eq. of water .			=156.75	
Nitrate of protox. lead .	111.6 1 eq.	+54.15 1 eq.	=165.75	$\overset{\cdot}{\mathrm{Pb}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Dinitrate of ditto . .	223.2 2 eq.	+54.15 1 eq.	=277.35	$2\overset{\cdot}{\mathrm{Pb}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Nitrate of protox. mercury	210 1 eq.	+54.15 1 eq.	=264.15	$\overset{\cdot}{\mathrm{Hg}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Do. in crystals with 18 or 2 eq. of water .			=282.15	
Nitrate of perox. mercury	218 1 eq.	+54.15 1 eq.	=272.15	$\overset{\cdot\cdot}{\mathrm{Hg}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Dinitrate of ditto .	436 2 eq.	+54.15 1 eq.	=490.15	$2\overset{\cdot\cdot}{\mathrm{Hg}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.
Nitrate of ox. silver .	116 1 eq.	+54.15 1 eq.	=170.15	$\overset{\cdot}{\mathrm{Ag}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}$.

Nitrate of Potassa.—This salt is generated spontaneously in the soil, and crystallizes upon its surface, in several parts of the world, and especially in the East Indies, whence the greater part of the nitre used in Britain is derived. In some parts of the continent, it is prepared artificially from a mixture of common mould or porous calcareous earth with animal and vegetable remains containing nitrogen. When a heap of these materials, preserved moist and in a shady situation, is moderately exposed to the air, nitric acid is gradually generated, and unites with the potassa, lime, and magnesia, which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potassa, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is probably generated under these circumstances by the nitrogen of the organic matters combining during putrefaction with oxygen of the atmosphere, a change which must be attributed to the affinity of oxygen for nitrogen, aided by that of nitric acid for alkaline bases. The nitre made in France is often said to be formed by this process; but the greater part is certainly obtained by lixiviation from certain kinds of plaster of old houses, where nitrate of lime is gradually generated.

Nitrate of potassa is a colourless salt, which crystallizes readily in six-sided prisms. Its taste is saline, accompanied with an impression of coolness. It requires for solution seven parts of water at 60°, and its own weight of boiling water. It contains no water of crystallization, but its crystals are never quite free from water lodged mechanically within them. At 616° it undergoes the igneous fusion, and like all the nitrates is decomposed by a red heat.

Nitre is chiefly employed in chemistry as an oxidizing agent, and in the formation of nitric acid. Its chief use in the arts is in making gunpowder, which is a mixture of nitre, charcoal, and sulphur. In the East Indies it is employed for the preparation of cooling mixtures:—an ounce of powdered nitre dissolved in five ounces of water reduces its temperature by fifteen degrees. It possesses powerful antiseptic properties, and is, therefore, much employed in the preservation of meat and animal matters in general.

Nitrate of Soda.—This salt is analogous in its chemical properties to the preceding compound. It sometimes crystallizes in oblique rhombic prisms; but it more commonly occurs as an obtuse rhombohedron, which is its primary form. (Mr. Brooke.) It is plentifully found in the soil in some parts of India; and at Atacama in Peru it covers large districts, and occurs in immense quantity. With charcoal and sulphur it forms a mixture which burns much slower than common gunpowder, and, therefore, cannot be substituted for nitre; but it may be advantageously used in the manufacture both of sulphuric and nitric acid. It is disposed to deliquesce in the air, and is soluble in twice its weight of cold water, and still more freely by the aid of heat.

Nitrate of Ammonia.—Nitrate of ammonia may be formed by neutralizing dilute nitric acid by carbonate of ammonia, and evaporating the solution. This salt may be procured in three different states, which have been described by Sir H. Davy. (Researches concerning the Nitrous Oxide.) If the evaporation is conducted at a temperature not exceeding 100°, the salt is obtained in prismatic crystals which contain one equivalent of water. If the solution is evaporated at 212°, fibrous crystals are procured; and if the heat be gradually increased to 300°, it forms a brittle compact mass on cooling. The fibrous and compact varieties still contain water, the former 8.2 per cent., and the latter 5.7. All these varieties deliquesce in a moist air, and are very soluble in water.

The change which nitrate of ammonia undergoes at a temperature varying between 400° and 500° has already been explained. (Page 174.) When heated to 600°, it explodes with violence, being resolved into water, nitrous acid, binoxide of nitrogen, and nitrogen. The fibrous variety was found by Davy to yield the largest quantity of protoxide of nitrogen. From one pound of this salt he procured nearly three cubic feet of the gas.

Nitrate of Baryta.—This salt is sometimes used as a reagent and for preparing pure baryta. It is easily prepared by digesting the native carbonate, reduced to powder, in nitric acid diluted with 8 or 10 times its weight of water. The salt crystallizes readily by evaporation in transparent anhydrous octohedrons, and is very apt to decrepitate by heat unless previously reduced to powder. It requires 12 parts of water at 60° and 3 or 4 of boiling water for solution, but is insoluble in alcohol. It undergoes the igneous fusion in the fire before being decomposed.

Nitrate of Strontia.—This salt may be made from strontianite in the same manner as the foregoing compound, to which it is exceedingly analogous. It commonly crystallizes in anhydrous octohedrons which undergo no change in a moderately dry atmosphere, and are insoluble in alcohol; but sometimes it contains 30 per cent. of water of crystallization, and then assumes the form of a prism with ten sides and two summits.

Nitrates of Lime and Magnesia.—These salts crystallize in hydrated prisms when their solutions are concentrated to the consistence of syrup, but the quantity of water which they contain is not ascertained. They deliquesce rapidly in the air, are very soluble in water, and are dissolved by alcohol, the nitrate of lime more freely than nitrate of magnesia.

Nitrate of Protoxide of Copper.—This salt is prepared by the action of nitric acid on copper. (Page 176.) It crystallizes, though with some difficulty, in prisms of a deep blue colour, which are very soluble in water and alcohol, and deliquesce on exposure to the air. The green insoluble subsalt, procured by exposing the neutral nitrate to a heat of 400°, or by dropping an alkali into a solution of that salt, the latter being in excess, is a trinitrate, consisting of three eq. of oxide of copper, one eq. of acid, and one eq. of water. When heated to redness it yields pure oxide of copper.

Nitarte of Protoxide of Lead.—This salt is formed by digesting litharge in dilute nitric acid, and crystallizes readily in octohedrons, which are anhydrous and almost always opaque. It has an acid reaction, but is neutral in composition.

A *dinitrate* was formed by Berzelius by adding to a solution of the neutral nitrate, a quantity of pure ammonia insufficient for separating the whole of the acid.

Nitrates of the Oxides of Mercury.—The *protonitrate* is conveniently formed by digesting mercury in nitric acid diluted with three or four parts of water, until the acid is saturated, and then allowing the solution to evaporate spontaneously in an open vessel. The solution always contains at first some nitrate of the peroxide, but if metallic mercury is left in the liquid, a pure protonitrate is gradually deposited. The salt thus formed has hitherto been regarded as the neutral protonitrate; but according to the analysis of M. C. Mitscherlich (Pog. Annalen, ix. 387), it is a subsalt, in which the protoxide and acid are in the ratio of 208 to 36. This result, however, requires confirmation. The neutral protonitrate is said by C. Mitscherlich to be obtained in crystals, by dissolving the former salt in pure water acidulated with nitric acid, and evaporating spontaneously without the contact of metallic mercury or uncombined oxide. These salts dissolve completely in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow subsalt is generated.

When mercury is heated in an excess of strong nitric acid, it is dissolved with brisk effervescence, owing to the escape of binoxide of nitrogen, and transparent prismatic crystals of the *pernitrate* are deposited as the solution cools. When put into hot water it is resolved into a soluble salt, the composition of which is unknown, and into a yellow *dinitrate* of the peroxide. (An. de Ch. et de Phys. xix.)

Nitrate of Oxide of Silver.—Silver is readily oxidized and dissolved by nitric acid diluted with two or three times its weight of water, forming a solution which yields transparent tabular crystals by evaporation. These crystals, which are anhydrous, undergo the igneous fusion at 426°, and yield a crystalline mass in cooling; but when the temperature reaches 600° or 700°, complete decomposition ensues, the acid being resolved into oxygen and nitrous acid, while metallic silver is left. When liquefied by heat, and received in small cylindrical moulds, it forms the *lapis infernalis* or *lunar caustic*, employed by surgeons as a cautery. The nitric acid appears to be the agent which destroys the animal texture, and the black stain is owing to the separation of oxide of silver. It is sometimes employed for giving a black colour to the hair, and is the basis of the indelible ink for marking linen.

The pure nitrate, whether fused or in crystals, is colourless and transparent, and does not deliquesce by exposure to the air; but common lunar caustic is dark and opaque, and dissolves imperfectly in water, owing to some of the nitrate being decomposed during its preparation. It is impure also, always containing nitrate of protoxide of copper, and frequently traces of gold. The pure salt is soluble in its own weight of cold, and in half its weight of hot water. It dissolves also in four times its weight of alcohol. Its aqueous solution, if preserved in clean glass vessels, undergoes little or no change even in the direct solar rays; but when exposed to light, especially to sunshine, in contact with paper, the skin, or any organic substance, a black stain is quickly produced, owing to decomposition of the salt and reduction of its oxide to the metallic state. This change is so constant, that nitrate of oxide of silver constitutes an extremely delicate test of the presence of organic matter, and has been properly recommended as such by Dr. Davy. Its solution is always kept in the laboratory as a test for chlorine and hydrochloric acid.

Nitrate of oxide of silver, even after fusion, reddens vegetable colouring matters; but it is quite neutral in composition.

NITRITES.

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. Nitrite of potassa is formed by heating nitre to redness, and removing it from the fire before the decomposition is complete. On adding a strong acid to the product, red fumes of nitrous acid are disengaged, a character which is common to all the nitrites. The nitrite of soda, baryta, and strontia, may be obtained in the same manner, and doubtless several others. Two nitrites of oxide of lead have been described in the Annales de Chimie, lxxxiii. by Chevreul and Berzelius. It is possible, however, that these compounds are hyponitrites.

CHLORATES.

The salts of chloric acid are very analogous to the nitrates. As the chlorates of the alkalies, alkaline earths, and most of the common metals are composed of one equivalent of chloric acid and one equivalent of a protoxide, $\overset{\cdot}{M}+\overset{\cdot\cdot\cdot\cdot\cdot}{Cl}$, it follows that the oxygen of the former to that of the latter is in the ratio of 1 to 5. The chlorates are decomposed by a red heat, nearly all of them being converted into metallic chlorides, with evolution of pure oxygen gas. They deflagrate with inflammable substances with greater violence than nitrates, yielding oxygen with such facility that an explosion is produced by slight causes. Thus, a mixture of sulphur with three times its weight of chlorate of potassa explodes when struck between two hard surfaces. With charcoal and the sulphurets of arsenic and antimony, this salt forms similar explosive mixtures; and with phosphorus it detonates violently by percussion. One of the mixtures, employed in the percussion locks for guns, consists of sulphur and chlorate of potassa, with which a little charcoal or gunpowder is mixed; but as the use of these materials is found corrosive to the lock, fulminating mercury is now generally preferred.

All the chlorates hitherto examined are soluble in water, excepting the chlorate of protoxide of mercury, which is of sparing solubility. These salts are distinguished by the action of strong hydrochloric and sulphuric acids, the former of which occasions the disengagement of chlorine and protoxide of chlorine, and the latter of peroxide of chlorine.

None of the chlorates are found native, and the only ones that require particular description are those of potassa and baryta.

Chlorate of Potassa.—This salt, formerly called *oxymuriate* or *hyperoxymuriate of potash*, is colourless, and crystallizes in four and six-sided scales of a pearly lustre. Its primary form is stated by Mr. Brooke to be an oblique rhombic prism. It is soluble in sixteen times its weight of water at 60°, and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° undergoes the igneous fusion. On increasing the heat almost to redness, effervescence ensues, and pure oxygen gas is disengaged, phenomena which have been explained in the section on oxygen. It can bear a heat of 660° without decomposition.

Chlorate of potassa is made by transmitting chlorine gas through a concentrated solution of pure potassa, until the alkali is completely neutralized. The solution, which, after being boiled for a few minutes, contains nothing but chloride of potassium and chlorate of potassa (page 211), is gently evaporated till a pellicle forms upon its surface, and is then allowed to cool. The greater part of the chlorate crystallizes, while the chloride remains in solution. The crystals, after being washed with cold water, may be purified by a second crystallization.

Chlorate of Baryta is of interest, as being the compound employed in the formation of chloric acid; and the readiest mode of preparing it is by the process of Mr. Wheeler. On digesting for a few minutes a concentrated solution of chlorate of potassa with a slight excess of silicated hydrofluoric acid, the alkali is precipitated in the form of an insoluble double fluoride of silicium and potassium, while chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which throws down the excess of silicated hydrofluoric acid, and chlorate of baryta is left in solution. By evaporation it yields prismatic crystals, which require for solution 4 times their weight of cold, and a still smaller quantity of hot water. They are composed of 76.7 parts or one eq. of baryta, 75.42 or one eq. of chloric acid, and 9 or one eq. of water.

Perchlorates.—The neutral protosalts of perchloric acid consist of one equivalent of acid and base, as is expressed by the formula $\dot{M}+\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{Cl}$. Most of these salts are deliquescent, very soluble in water, and soluble in alcohol; four only were found by Serullas to be not deliquescent,—the perchlorates of potassa, ammonia, protoxide of lead, and protoxide of mercury. When heated to redness they yield oxygen gas and metallic chlorides; and they are distinguished from the chlorates by not acquiring a yellow tint on the addition of hydrochloric acid. The perchlorate of potassa is prepared from the chlorate by the action of heat and sulphuric acid, as already mentioned. (Page 218.) It is the most insoluble of the perchlorates, and on this account perchloric acid precipitates potassa from its salts, being a test of about the same delicacy as tartaric acid. The other perchlorates are made by neutralizing the base with perchloric acid. The solubility in alcohol of the perchlorates of baryta, soda, and oxide of silver, is a property which the analytical chemist may avail himself of in analysis for the separation of potassa and soda from each other.

IODATES.

From the close analogy in the composition of chloric and iodic acids, it follows that the general character of the iodates must be similar to that of the chlorates. Thus in all neutral protiodates the oxygen contained in the oxide and acid is in the ratio of 1 to 5. They form deflagrating mixtures with combustible matters; and on being heated to low redness, oxygen gas is disengaged and a metallic iodide remains. As the affinity of iodine for metals is less energetic than that of chlorine, many of the iodates part with iodine as well as oxygen when heated, especially if a high temperature is employed.

The iodates are easily recognized by the facility with which their acid is decomposed by deoxidizing agents. Thus, the sulphurous, phosphorous, hydrochloric, and hydriodic acids, deprive iodic acid of its oxygen, and set iodine at liberty. Hydrosulphuric acid also decomposes the acid of these salts; and hence an iodate of potassa may be converted into the iodide of potassium by transmitting a current of hydrosulphuric acid gas through its solution.

None of the iodates have been found native. They are all of very sparing solubility, or actually insoluble in water, excepting the iodates of the alkalies.

Iodate of Potassa.—This salt may be procured by adding iodine to a concentrated hot solution of pure potassa, until the alkali is completely neutralized. The liquid, which contains an iodate and iodide (page 227), is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by repeated portions of boiling alcohol. The iodate, which is insoluble in that menstruum, is left, while the iodide of potassium is dissolved. A better process has been recommended by M. Henry, jun., founded on the property which iodide of potassium possesses, of absorbing oxygen while in the act of escape from decomposing chlorate of potassa. For this purpose iodide of potassium is fused in a capacious Hessian crucible, and when, after removal from the fire, it is yet semi-fluid, successive portions of pulverized chlorate of potassa are projected into it, stirring well after each addition. The materials froth up considerably, and when the action is over, a white, opaque, cellular mass remains, easily separable from the crucible: tepid water dissolves out the chloride of potassium, and leaves the iodate. Convenient proportions are one part of iodide of potassium and rather more than one and a half of chlorate of potassa. (Journ. de Pharmacie, July, 1832.)

All the insoluble iodates may be procured from this salt by double decomposition. Thus iodate of baryta may be formed by mixing chloride of barium with a solution of iodate of potassa.

A biniodate of potassa has been described by Serullas. It is formed by incompletely neutralizing a hot solution of chloride of iodine with potassa or its carbonate, and setting it aside to cool. A peculiar compound of chloride of potassium and biniodate of potassa falls; but on dissolving this substance, filtering and exposing the solution to a temperature of 77°, the biniodate is gradually deposited in right rhombic prisms terminated by dihedral summits. It is soluble in 75 times its weight of water at 59°.

A teriodate may be formed by mixing a large excess of sulphuric acid with a moderately dilute solution of iodate of potassa. On evaporating at 77°, the teriodate is deposited in regular rhomboidal crystals, which require 25 times their weight of water at 60° for solution.

Serullas states that the compound of chloride of potassium and biniodate of potassa, above mentioned, may be formed by the action of hydrochloric acid on iodate of potassa. By spontaneous evaporation it is obtained, sometimes in brilliant, transparent, elongated prisms, and at other times in hexagonal laminæ; but generally it crystallizes in right quadrangular prisms with their lateral edges truncated, and terminated by four-sided summits. (An. de Ch. et de Ph. xliii. 113.)

Bromates.—These compounds have may characters common with the chlorates and iodates; but hitherto they have been but partially examined.

PHOSPHATES.

In studying these salts, the reader must bear in mind that there are three isomeric modifications of the same acid, which have been described under the names of *phosphoric*, *pyrophosphoric*, and *metaphosphoric acid* (page 202); and, therefore, it will be necessary to have three corresponding families of salts, the *phosphates*, *pyrophosphates*, and *metaphosphates*. This distinction, and the other facts lately recorded by Mr. Graham, render it necessary either to change the names of the phosphates or to retain their old names in opposition to the principles of nomenclature. The most consistent conduct will be to describe each salt under its scientific name, and add at the same time its ordinary one. An equivalent of each of the three acids, is a compound of 31.4 parts or two eq. of phosphorus + 40 parts or five eq. of oxygen = 71.4, expressed by the formula $\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$. To form a salt *neutral in composition*, one equivalent of an alkaline base is requisite; and in the case of any protoxide, indicated by $\dot{M}$, the general formula will be $\dot{M}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$. If two equivalents of a protoxide are united with one of the acid, we have a *disalt*, $2\dot{M}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$; and if three eq. of a base combine with one eq. of the acid, it is a *trisalt*, $3\dot{M}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$. It seems also that water plays the part of an alkaline base towards each of the three acids, either alone or conjointly with another base: the salts with such compound bases can scarcely be viewed in the light of double salts (page 434); since the two bases act together as one electro-positive element.

All the protophosphates which are neutral in composition, are soluble in water, and redden litmus paper; whence they are commonly called superphosphates. The triphosphates, except those of the pure alkalies, are either sparingly soluble or insoluble in water; but they are all dissolved by dilute nitric or phosphoric acid, being converted into the soluble phosphates. All the triphosphates with fixed and strong bases bear a red heat without change;

but the phosphates and diphosphates, to judge from experiments on the soda salts, are converted into metaphosphates and pyrophosphates. Most of the phosphates of the second class of metals are resolved into phosphurets by the conjoint agency of heat and combustible matter. The phosphates of the alkalies are only partially decomposed under these circumstances, and the phosphates of baryta, strontia, and lime undergo no change.

The presence of a soluble phosphate may be distinguished by the tests already mentioned (page 203) for phosphoric acid. The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potassa or soda; the acid uniting with the alkali so as to form a soluble phosphate: the earthy phosphates, indeed, are decomposed with difficulty, requiring continued ebullition, and should preferably be fused with an alkaline carbonate, like an insoluble sulphate.

Several phosphates are met with in nature, such as those of lime, alumina, and the oxides of manganese, iron, uranium, copper, and lead.

The composition of the principal phosphates is given in the following table:—

Names.		Base.		Acid.		Equiv.	Formulæ.
Triphosphate of soda .		93.9	3 eq.	+71.4	1 eq.	=165.3	$3\overset{\cdot}{Na}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 216 or 24 eq. of water .						=381.3	
Triphosph. soda and basic water .	Soda Water	62.6 9	2 eq. 1 eq.	+71.4	1 eq.	=143	$\overset{\cdot}{Na}^2\overset{\cdot}{H}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 216 or 24 eq. of water .						=359	
Do. 126 or 14 eq. of water .						=269	
Acid triphos. soda and basic water	Soda Water	31.3 18	1 eq. 2 eq.	+71.4	1 eq.	=120.7	$\overset{\cdot}{Na}\overset{\cdot}{H}^2+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 18 or 2 eq. of water .						=138.7	
Triphosphate of potassa		141.45	3 eq.	+71.4	1 eq.	=212.85	$3\overset{\cdot}{K}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Diphosphate do		94.3	2 eq.	+71.4	1 eq.	=165.7	$2\overset{\cdot}{K}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Phosphate do		47.15	1 eq.	+71.4	1 eq.	=118.55	$\overset{\cdot}{K}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 18 or 2 eq. of water . .						=136.55	
Phosphate of soda and ammonia	Soda Ammon.	31.3 17.15	1 eq. 1 eq.	+71.4	1 eq.	=119.85	$\overset{\cdot}{Na}H^8N+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 90 or 10 eq. of water .						=209.85	
Diphosphate of ammonia		34.3	2 eq.	+71.4	1 eq.	=105.7	$2H^3N+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 27 or 3 eq. of water .						=132.7	
Phosphate of ammonia		17.15	1 eq.	+71.4	1 eq.	=88.55	$H^3N+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Do. in crystals with 27 or 3 eq. of water .						=115.55	
Bone phosphate of lime		228	8 eq.	+214.2	3 eq.	=442.2	$8\overset{\cdot}{Ca}+3\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Triphosphate do. .		85.5	3 eq.	+ 71.4	1 eq.	=156.9	$3\overset{\cdot}{Ca}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Diphosphate do. .		57	2 eq.	+ 71.4	1 eq.	=128.4	$2\overset{\cdot}{Ca}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$
Phosphate do. .		28.5	1 eq.	+ 71.4	1 eq.	= 99.9	$\overset{\cdot}{Ca}+\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{P}}$

The triphosphate of baryta, strontia, protoxides of manganese, iron, copper, lead, silver, &c. precisely correspond to the triphosphate of lime, simply substituting three equivalents of those oxides. These oxides in like manner form soluble phosphates analogous in composition to that of lime.

Triphosphate of Soda.—This salt, lately described by Mr. Graham as the *subsesquiphosphate*, is made by adding pure soda to a solution of the succeeding compound until the liquid feels soapy to the fingers, an excess of soda not being injurious. The liquid is then evaporated until a pelicle appears, and the crystals which form on cooling are quickly redissolved in water and recrystallized. Though the crystals do not change in the air, the solution absorbs carbonic acid, and the resulting carbonate of soda adheres to the triphosphate.

This salt crystallizes in colourless six-sided slender prisms, which have a strong alkaline taste and reaction, require 5 times their weight of water at 60°, and still less of hot water, for solution, and at 170° fuse in their water of crystallization. They may be exposed to a red heat without losing the characters of a phosphate. The feeblest acids deprive the salt of one-third of its soda.

When this salt is mixed in solution with nitrate of oxide of silver in excess, there is an exact interchange of elements, such that

$$\begin{array}{llcll} \text{1 eq. triphosphate of soda} & 3\dot{\mathrm{Na}}\underline{+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}} & & \text{1 eq. triphosphate of silver} & 3\dot{\mathrm{Ag}}\underline{+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}} \\ & & \text{yield} & & \\ \text{and 3 eq. nitrate of silver} & 3(\dot{\mathrm{Ag}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}) & & \text{and 3 eq. nitrate of soda} & 3(\dot{\mathrm{Na}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}). \end{array}$$

The resulting solution is, therefore, quite neutral. The triphosphate of oxide of lead, and other insoluble triphosphates, may be prepared in like manner.

Triphosphate of Soda and Basic Water.—This salt is the most common of the phosphates, being manufactured on a large scale by neutralizing with carbonate of soda the acid phosphate of lime procured by the action of sulphuric acid on burned bones (page 198). It is generally described as the neutral phosphate of soda, and for distinction's sake is sometimes termed *rhombic phosphate*, from its crystals having the form of oblique rhombic prisms.

This salt crystallizes best out of an alkaline solution; but however prepared, it is always alkaline to test paper, and requires a considerable quantity of acid before losing its alkalinity. The crystals effloresce on exposure to the air, and require four times their weight of cold, and twice their weight of hot water for solution. It often contains traces of sulphuric acid, from which it may be purified by repeated solution and crystallization. When mixed with nitrate of oxide of silver, the interchange of elements is such that

$$\begin{array}{llcll} \text{1 eq. rhombic phosphate} & \dot{\mathrm{Na}}^2\dot{\mathrm{H}}\underline{+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}} & & \text{1 eq. triphosp. of silver} & 3\dot{\mathrm{Ag}}\underline{+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}}. \\ & & \text{yield} & & \\ \text{and 3 eq. nitrate of silver} & 3(\dot{\mathrm{Ag}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}.) & & \text{and 2 eq. nitrate of soda} & 2(\dot{\mathrm{Na}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{N}}). \end{array}$$

The yellow triphosphate of oxide of silver falls exactly as with the former salt, but one equivalent of nitric acid is left free in the solution.

When a solution of the rhombic phosphate is evaporated at a temperature of 90°, it crystallizes with 14 instead of 24 equivalents of water, and the crystals differ, as might be expected, from the other salt in figure, and are permanent in the air. Both salts lose their basic water at a red heat, and are converted into a pyrophosphate.

Acid Triphosphate of Soda and Water.—This salt, commonly called *biphosphate of soda* from its acid reaction, may be formed by adding phosphoric acid to a solution of carbonate of soda, or to either of the preceding phosphates, until it ceases to give a precipitate with chloride of barium. Being very soluble in water, the solution must be concentrated in order that it may crystallize. This salt is capable of yielding two different kinds of crystals without varying its composition. The more unusual form, isomorphous with binarseniate of soda, is a right rhombic prism, the smaller lateral edge of which is 78° 30′, terminated by pyramidal planes. The primary form of its ordinary crystals is a right rhombic prism, the larger angle of which is 93° 54′.

The crystals of this salt consist, as stated at page 451, of $\dot{\mathrm{Na}}\dot{\mathrm{H}}^{2}\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}}+2\dot{\mathrm{H}}$. When heated to 212° the water of crystallization is expelled, and the anhydrous salt remains, still yielding a yellow precipitate with silver when neutralized by ammonia; but if exposed to a heat of 400°, it loses half its basic water, being reduced to $\dot{\mathrm{Na}}\dot{\mathrm{H}}\underline{\overset{\cdot\cdot\cdot\cdot\cdot}{\mathrm{P}}}$, and has the character of dipyrophosphate of soda. At a red heat it is converted into metaphosphate of soda.

Triphosphate of Potassa.—Mr. Graham formed this salt by adding caustic potassa in excess to a solution of phosphoric acid, as well as by fusing phosphoric acid with a slight excess of carbonate of potassa. He obtained it in acicular crystals, which were very soluble in water but not deliquescent.

Diphosphate of Potassa.—This salt may be prepared by neutralizing the superphosphate of lime from bones with carbonate of potassa. It is deliquescent, and has not been obtained in regular crystals.

Phosphate of Potassa may be formed by adding phosphoric acid to carbonate of potassa until the liquid ceases to give a precipitate with chloride of barium, and setting it aside to crystallize. The primary form of the crystals is an octohedron with a square base; but they usually occur in square prisms terminated by the planes of their primary form. They are acid to test paper.

When this compound is neutralized by carbonate of soda, and the solution set to crystallize, a phosphate of soda and potassa is deposited in crystals, the primary form of which is an oblique rhombic prism, which frequently occurs without any modification.

Phosphate of Soda and Ammonia.—This salt is easily prepared by mixing together one equivalent of hydrochlorate of ammonia and two equivalents of the rhombic phosphate of soda, each being previously dissolved in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while chloride of sodium remains in solution. Their primary form is an oblique rhombic prism. This salt has been long known by the name of *microcosmic salt*, and is much employed as a flux in experiments with the blowpipe. When heated it parts with its water and ammonia, and a very fusible metaphosphate of soda remains.

Diphosphate of Ammonia.—This salt is formed by adding ammonia to concentrated phosphoric acid until a precipitate appears. On applying heat, the precipitate is dissolved, and on abandoning the solution to itself, the neutral salt crystallizes. The primary form of the crystals is an oblique rhombic prism, the smaller angle of which is 84° 30′. They often occur in rhombic prisms with dihedral summits. (Mitscherlich.)

The *phosphate* is made in the same manner as the phosphate of potassa. The crystals are less soluble than the diphosphate, and undergo no change on exposure to the air. Their primary form is an octohedron with a square base; but the right square prism, terminated by the faces of the primary form, is the most frequent.

Phosphates of Lime.—The peculiar compound called the *bone phosphate*, exists in bones after calcination, and falls as a gelatinous precipitate on pouring chloride of calcium into a solution of the rhombic phosphate of soda, or on adding ammonia to a solution of any phosphate of lime in acids.

Triphosphate of Lime cannot be formed by precipitation, but occurs in hexagonal prisms in the mineral called *apatite.*

Diphosphate of Lime, commonly called *neutral phosphate*, falls as a granular precipitate, consisting of fine crystalline particles, when the rhombic phosphate of soda is added in solution drop by drop to chloride of calcium in excess. The residual liquid reddens litmus, owing to a small quantity of triphosphate of lime being generated.

Phosphate of Lime, called the *biphosphate* from its acid reaction, is formed by dissolving either of the preceding salts in a slight excess of phosphoric acid. The compound is deliquescent, very soluble, and crystallizes with great difficulty. It exists in the urine. The solution formed by the action of sulphuric acid on bones is probably a compound of lime with two or more equivalents of phosphoric acid, being really a *superphosphate*.

Phosphates of Magnesia.—The *diphosphate*, $2\dot{\mathrm{Mg}}+\overset{\therefore\cdot}{\underline{\mathrm{P}}}$, is formed by mixing hot saturated solutions of the rhombic phosphate of soda and sulphate of magnesia, and separates on cooling in small crystals which contain fourteen equivalents of water to one of the anhydrous salt. The *triphosphate* is principally formed when the solutions are intermixed in the cold. These salts have been but little examined.

The *phosphate of ammonia and magnesia* subsides as a pulverulent granular precipitate from neutral or alkaline solutions containing phosphoric acid, ammonia, and magnesia. It is readily dissolved by acids, and is sparingly soluble in pure water, especially when carbonic acid is present; but it is insoluble in a solution of most neutral salts, such as hydrochlorate of ammonia. It constitutes one variety of urinary concretions. According to Berzelius it consists of

Phosphoric acid . .	71.4	1 eq.	$\overset{\therefore\cdot}{\underline{\mathrm{P}}}$.
Magnesia . . .	41.4	2 eq.	$2\dot{\mathrm{Mg}}$.
Ammonia . . .	34.3	2 eq.	$2(3\mathrm{H}+\mathrm{N})$.
Water	90	10 eq.	$10\dot{\mathrm{H}}$.

The mode in which these elements are arranged is unknown. When heated to redness it loses its water and ammonia, and the residue is diphosphate of magnesia, which contains 36.67 per cent. of pure magnesia. At a strong red heat it fuses, and appears when cold as a white enamel.

When the materials for forming the preceding salt are mixed while hot, small acicular crystals subside on cooling, which are said by Berzelius to contain less of the two bases than the other salt.

Phosphates of Protoxide of Lead.—The *triphosphate* is precipitated when acetate of oxide of lead is mixed with a solution of the rhombic phosphate of soda, acetic acid being set free. The *diphosphate* is best formed by adding the rhombic phosphate of soda gradually to a hot solution of chloride of lead.

The nitrate should not be used for the purpose, as it combines with the precipitate. Both these phosphates are white, and are frequently formed at the same time. The diphosphate fuses readily into a yellow bead, which in cooling acquires crystalline facettes.

Triphosphate of Oxide of Silver.—This compound subsides, of a characteristic yellow colour (page 203), when the rhombic phosphate of soda is mixed in solution with nitrate of oxide of silver, nitric acid being set free at the same time. It is apt to retain some of the nitrate in combination. This salt is very soluble in nitric and phosphoric acid, forming the soluble phosphate, and in ammonia. By exposure to light it is speedily blackened; but when protected from this agent, it yields on drying an anhydrous yellow powder, which has a specific gravity of 7.321 (Stromeyer). Its colour changes on the application of heat to a reddish-brown, but its original tint returns on cooling. It bears a red heat without fusion: at a white heat it fuses, and if kept for some time in a fused state a portion of pyrophosphate is generated.

PYROPHOSPHATES.

The discovery of these salts by Dr. Clark has also been mentioned (page 203). That modification of phosphoric acid, termed *pyrophosphoric acid*, is procured by forcing with the aid of heat phosphoric acid to combine with two equivalents either of water or some fixed base. The only pyrophosphates which have as yet been studied are those of soda and oxide of silver. These salts are thus constituted:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Dipyrophosphate of soda . .	62.6 2 eq.	+ 71.4 1 eq.	=134	$2\dot{\mathrm{Na}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$
Do. in crystals with 90 or 10 eq. of water .			=224	
Acid dipyrophos. soda and basic water	Soda 31.3 1 eq. Water 9 1 eq.	+ 71.4 1 eq.	=111.7	$\dot{\mathrm{Na}}\dot{\mathrm{H}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$
Pyrophosphate of soda .	31.3 1 eq.	+ 71.4 1 eq.	=102.7	$\dot{\mathrm{Na}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$
Dipyrophos. oxide of silver .	232 2 eq.	+ 71.4 1 eq.	=303.4	$2\dot{\mathrm{Ag}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$

Dipyrophosphate of Soda.—This is the compound first prepared by Dr. Clark from the rhombic phosphate (page 203), by expelling its basic water. When the residual mass is dissolved in water and set to evaporate, crystals are obtained, having the outline of an irregular six-sided prism, derived from a rhombic prism. These crystals are permanent in the air, much less soluble in water than the original rhombic phosphate, and quite neutral to test paper. Ignited with carbonate of soda, a phosphate is reproduced, because the acid is forced to unite with three equivalents of a base.

Dipyrophosphate of soda is permanent both in crystals and in solution in the cold; but by long boiling, or quickly when boiled with an acid, a phosphate is reproduced. With a salt of lead it yields a white dipyrophosphate of oxide of lead; and on washing the precipitate and decomposing by hydrosulphuric acid gas, a solution of pyrophosphoric acid is obtained, which again forms dipyrophosphate of soda when neutralized with soda.

The oxides of most metals of the second class yield with pyrophosphoric acid insoluble or sparingly soluble salts, which may be prepared by double decomposition with dipyrophosphate of soda. It should be held in view, however, as Stromeyer has remarked, that most of these salts are more or less soluble in an excess of dipyrophosphate of soda; and that some of them, such as the dipyrophosphate of the oxides of lead, copper, nickel, cobalt, uranium, bismuth, manganese, and mercury, are dissolved by it with great facility.

Acid Dipyrophosphate of Soda and Water.—This salt is formed by exposing, as stated at page 453, the acid triphosphate to a heat of 400°, when it loses one half of its basic water, and acquires the character of a pyrophosphate. This salt dissolves readily in water, has an acid reaction, and has not been obtained in crystals.

Pyrophosphate of Soda.—When the preceding salt, $\dot{\mathrm{Na}}\dot{\mathrm{H}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$, is heated to 600° or a little higher, it loses its basic water, and yet the acid does not lose the character of pyrophosphoric acid. It is left, therefore, as a simple pyrophosphate of soda, $\dot{\mathrm{Na}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$. On adding water, part of it dissolves, and part is left as an insoluble white powder. The solution is *quite neutral to test paper*, but on adding nitrate of oxide of silver, the dipyrophosphate of that oxide falls, and free nitric acid remains in solution. The soluble and insoluble pyrophosphate of soda appear identical in composition; and the former at a heat just short of redness may be wholly converted into the latter.

Dipyrophosphate of Oxide of Silver.—This salt is readily formed by double decomposition with dipyrophosphate of soda and nitrate of oxide of silver, the residual liquid being quite neutral to test paper. It falls as a snow-white granular precipitate, which fuses readily at a heat short of incandescence into a dark brown liquid, which becomes a crystalline enamel on cooling.

METAPHOSPHATES.

The only metaphosphates which have yet been examined, are those of soda, baryta, and oxide of silver, which are thus constituted:—

Names.		Base.	Acid.	Equiv.	Formulæ.
Metaphosphate of soda . .		31.3	1 eq.+71.4	1 eq.=102.7	$\overset{\cdot}{\mathrm{Na}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$
Do.	baryta . .	76.7	1 eq.+71.4	1 eq.=148.1	$\overset{\cdot}{\mathrm{Ba}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$
Do.	ox. silver	116	1 eq.+71.4	1 eq.=187.4	$\overset{\cdot}{\mathrm{Ag}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$
Submetaphos.	do.	348	3 eq.+142.8	2 eq.=490.8	$3\overset{\cdot}{\mathrm{Ag}}+2\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{P}}}$

Metaphosphate of Soda.—When the pyrophosphate or acid dipyrophosphate of soda is heated to low redness, it fuses, and on cooling becomes a transparent glass, which deliquesces in a damp air, and is very soluble. The solution has a feeble acid reaction. When mixed with nitrate of oxide of silver, the metaphosphate of that oxide falls in gelatinous flakes, wholly unlike the pyrophosphate, and aggregates together as a soft solid when heated to near 212°. The metaphosphate of soda does not change by keeping, and has not hitherto been made to crystallize. When its solution is evaporated, and kept for some time at 400°, it is reconverted into the acid dipyrophosphate of soda and basic water. All the preceding facts are drawn from Mr. Graham's essay. (Phil. Trans. 1833, Part ii.)

Metaphosphate of Baryta falls in gelatinous flakes on adding metaphosphate of soda to a solution of chloride of barium, the latter being in excess as the soda salt dissolves the precipitate. By long continued boiling, metaphosphate of baryta is at length dissolved, and at the same time converted into a phosphate.

The *metaphosphate of silver* is obtained by precipitation, as above stated. When put, while moist, into boiling water, part of its acid is removed, and the submetaphosphate is generated.

ARSENIATES.

Arsenic acid resembles the phosphoric in composition and in many of its properties, and all the protarseniates of neutral composition are represented by the formula $\overset{\cdot}{\mathrm{M}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{As}}}$, the oxygen of the oxide and acid being as 1 to 5. These salts, like the phosphates, are soluble in water and redden litmus, whence they are commonly considered as bisalts. The diarseniates, $2\overset{\cdot}{\mathrm{M}}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{\mathrm{As}}}$, in which the oxygen of the base and acid is as 2 to 5, are usually termed neutral arseniates. Arsenic acid has a strong tendency to the formation of triarseniates. Both these series of subsalts, except those with the alkalies, are of sparing solubility in water; but they are dissolved by phosphoric or nitric acid, as well as most acids which do not precipitate the base of the salt.

Many of the arseniates bear a red heat without decomposition, or being otherwise modified in their characters; but they are all decomposed when heated to redness along with charcoal, metallic arsenic being set at liberty. The arseniates of the fixed alkalies and alkaline earths require a rather high temperature for reduction; while the arseniates of the second class of metals, as of lead and copper, are easily reduced in a glass tube by means of a spirit-lamp without danger of melting the glass. Of all the arseniates that of oxide of lead is the most insoluble.

The soluble arseniates are easily recognized by the tests described in the section on arsenic (page 357); and the insoluble arseniates, when boiled in a strong solution of the fixed alkaline carbonates, are deprived of their acid, which may then be detected in the usual manner. The free alkali, however, should first be exactly neutralized by pure nitric acid.

The arseniates of lime, and of the oxides of nickel, cobalt, copper, and lead, are natural productions.

The composition of the principal arseniates is contained in the following table:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Triarseniate of soda	93.9 3 eq.	+ 115.4 1 eq.	=209.3	$3\dot{Na}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Do. in crystals with	216 or 24 eq. of water		=425.3	
Triarsen. soda and basic water — soda	62.6 2 eq.	+115.4 1 eq.	=187	$\dot{Na}^2\dot{H}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
— water	9 1 eq.			
Do. in crystals with	216 or 24 eq. of water		=403	
Do. in crystals with	126 or 14 eq. of water		=313	
Acid triarsen. soda and basic water — soda	31.3 1 eq.	+ 115.4 1 eq.	=164.7	$\dot{Na}\dot{H}^2+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
— water	18 2 eq.			
Do. in crystals with	18 or 2 eq. of water		=182.7	
Triarseniate of potassa .	141.45 3 eq.	+ 115.4 1 eq.	=256.85	$3\dot{K}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Diarseniate do. . .	94.3 2 eq.	+ 115.4 1 eq.	=209.7	$2\dot{K}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Arseniate of potassa .	47.15 1 eq.	+ 115.4 1 eq.	=162.55	$\dot{K}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Do. in crystals with	18 or 2 eq. of water		=180.55	
Diarseniate of ammonia	34.3 2 eq.	+ 115.4 1 eq.	=149.7	$2H^3N+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Do. in crystals with	27 or 3 eq. of water		=176.7	
Arseniate of ammonia .	17.15 1 eq.	+ 115.4 1 eq.	=132.55	$H^3N+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Do. in crystals with	27 or 3 eq. of water		=159.55	
Triarseniate of baryta .	230.1 3 eq.	+ 115.4 1 eq.	=345.5	$3\dot{Ba}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Diarseniate do. . .	153.4 2 eq.	+ 115.4 1 eq.	=268.8	$2\dot{Ba}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Arseniate do. . .	76.7 1 eq.	+ 115.4 1 eq.	=192.1	$\dot{Ba}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Triarseniate of lime .	85.5 3 eq.	+ 115.4 1 eq.	=200.9	$3\dot{Ca}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Diarseniate do. . .	57 2 eq.	+ 115.4 1 eq.	=172.4	$2\dot{Ca}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$
Arseniate do. . .	28.5 1 eq.	+ 115.4 1 eq.	=143.9	$\dot{Ca}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{As}}$

Names.	Base.	Acid.	Equiv.	Formulæ.
Triarseniate of protox. lead	334.8 3 eq.	+ 115.4 1 eq.	= 450.2	$3\dot{Pb}+\underline{\overset{\cdot\,\cdot}{\overset{\cdot\,\cdot\,\cdot}{As}}}$
Diarseniate do. .	223.2 2 eq.	+ 115.4 1 eq.	= 338.6	$2\dot{Pb}+\underline{\overset{\cdot\,\cdot}{\overset{\cdot\,\cdot\,\cdot}{As}}}$
Triarseniate of ox. silver .	348 3 eq.	+ 115.4 1 eq.	= 463.4	$3\dot{Ag}+\underline{\overset{\cdot\,\cdot}{\overset{\cdot\,\cdot\,\cdot}{As}}}$

Arseniates of Soda.—The triarseniate is made in the same manner as triphosphate of soda, with which it is isomorphous. At 60°, 100 parts of water dissolve 28 of the crystals, and still more by the aid of heat. At 186° they fuse in their water of crystallization.

The triarseniate of soda and basic water corresponds precisely in form and constitution with the corresponding phosphate, and like it parts with its last equivalent of water at a red heat; but does not, on losing it, receive any change in its characters. It is efflorescent and alkaline to test paper, and crystallizes best out of an alkaline solution. It is prepared by adding soda or its carbonate in slight excess to a solution of arsenic acid. The salt with fourteen equivalents of water coincides with the corresponding phosphate.

The acid triarseniate of soda and basic water is prepared like the corresponding phosphate.

The same observation applies to the arseniates of potassa and ammonia, each having its isomorphous phosphate. The triarseniate of potassa crystallizes in needles and with difficulty, like the corresponding triphosphate. The arseniate of potassa may be formed by heating nitre to redness mixed with an equal weight of arsenious acid.

The double arseniate of potassa and soda agrees in form and composition with the phosphate of those bases.

Arseniates of Baryta.—The triarseniate is best prepared by gradually adding in solution triarseniate of soda to chloride of barium in excess, and falls as a pulverulent heavy precipitate, which is apt to contain a little diarseniate of baryta as well as the soda salt, and should, therefore, be well washed with boiling water. On adding chloride of barium to an excess of triarseniate of soda, the latter salt always falls with the precipitate.

To prepare the diarseniate a solution of the rhombic triarseniate of soda is added drop by drop to chloride of barium in solution, when the *diarseniate* of baryta soon appears in white crystalline scales, which contain four equivalents of water. On reversing the process by adding chloride of barium to the arseniate, the precipitate is a mixture of the triarseniate and diarseniate of baryta. By the continued action of hot water on the diarseniate, it is partly changed into the soluble arseniate and insoluble triarseniate. The soluble arseniate is obtained by dissolving either of the two former salts, in a moist state, by dilute arsenic acid.

Arseniates of Lime.—The three salts analogous to those of baryta are obtained by precisely similar processes. The diarseniate occurs in silky acicular crystals as a rare mineral named *pharmacolite*, which contains six equivalents of water.

Arseniates of Protoxide of Lead.—The triarseniate is formed by adding in solution acetate of oxide of lead gradually to an excess of triarseniate of soda. The same salt falls when acetate of oxide of lead and the rhombic triarseniate of soda are intermixed, acetic acid being set free. It is a white very insoluble powder, which at a low red heat acquires a yellow tint, which it loses again on cooling.

The diarseniate may be made by a similar process as for forming the diphosphate, and is a white insoluble, easily fusible powder.

Triarseniate of Oxide of Silver.—This salt falls as a brick-red powder when nitrate of oxide of silver is mixed in solution with triarseniate of soda or the rhombic triarseniate, in the latter case nitric acid being set free. It is apt to retain some of the nitrate, which cannot be removed by washing; a property which the yellow phosphate of oxide of silver also possesses.

ARSENITES.

These salts have as yet been but little examined. The arsenites of potassa, soda, and ammonia may be prepared by acting with those alkalies on arsenious acid: they are very soluble in water, have an alkaline reaction, and have not been obtained in regular crystals. Most of the other arsenites are insoluble, or sparingly soluble, in pure water; but they are dissolved by an excess of their own acid, with great facility by nitric acid, and by most other acids with which their bases do not form insoluble compounds. The insoluble arsenites are easily formed by double decomposition.

All the arsenites are decomposed when heated in close vessels, the arsenious acid being either dissipated in vapour, or converted, with disengagement of some metallic arsenic, into arseniates. Heated with charcoal or black flux, the acid is reduced with facility. (Page 357.)

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of oxide of silver when mixed with the nitrate of that base, and a green arsenite of protoxide of copper, *Scheele's green*, with sulphate of that oxide. When acidulated with acetic or hydrochloric acid, hydrosulphuric acid causes the formation of orpiment. The insoluble arsenites are all decomposed when boiled in a solution of carbonate of potassa or soda.

The arsenite of potassa is the active principle of Fowler's arsenical solution.

CHROMATES.

The salts of chromic acid are mostly either of a yellow or red colour, the latter tint predominating whenever the acid is in excess. The chromates of oxides of the second class of metals are decomposed by a strong red heat, by which the acid is resolved into the green oxide of chromium and oxygen gas; but the chromates of the fixed alkalies sustain a very high temperature without decomposition. They are all decomposed without exception by the united agency of heat and combustible matter. The neutral chromates of protoxides are similar in constitution to the sulphates, being formed of one equivalent of the base and one of chromic acid, the formula being $\dot{\mathrm{M}}+\overset{\cdots}{\mathrm{Cr}}$.

The chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in hydrochloric acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green solution of the chloride of chromium being generated.

The only native chromate hitherto discovered is the red dichromate of protoxide of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

Chromates of Potassa.—The neutral chromate from which all the compounds of chromium are directly or indirectly prepared, is made by heating to redness the native oxide of chromium and iron, commonly called *chromate of iron*, with nitrate of potassa, when chromic acid is generated, and unites with the alkali of the nitre. The object to be held in view is to employ so small a proportion of nitre, that the whole of the alkali may combine with chromic acid, and constitute a neutral chromate, which is easily obtained pure by solution in water and crystallization. For this purpose the chromate of iron is mixed with about a fifth of its weight of nitre, and exposed to a strong heat for a considerable time; and the process is repeated with those portions of the ore which are not attacked in the first operation. It is deposited from its solution in small prismatic anhydrous crystals of a lemon-yellow colour, the primary form of which, according to Mr. Brooke, is a right rhombic prism.

Chromate of potassa has a cool, bitter, and disagreeable taste. It is soluble to great extent in boiling water, and in twice its weight of that liquid at 60°; but it is insoluble in alcohol. It has an alkaline reaction, and on this account M. Tassaert* regards it as a subsalt; but Dr. Thomson has proved that it is neutral in composition, consisting of 52 parts or one equivalent of chromic acid, and 47.15 parts or one equivalent of potassa.†

Bichromate of potassa, which is made in large quantity at Glasgow for dyeing, is prepared by acidulating the neutral chromate with sulphuric or still better with acetic acid, and allowing the solution to crystallize by spontaneous evaporation. When slowly formed it is deposited in four-sided tabular crystals, the primary form of which is an oblique rhombic prism. They have an exceedingly rich red colour, are anhydrous, and consist of one equivalent of the alkali, and two equivalents of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60°, and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta and oxides of zinc, lead, mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of chromate of potassa. The three former are yellow, the fourth orange-red, and the fifth deep red or purple. The yellow chromate of lead, which consists of one equivalent of acid and one equivalent of oxide, is now extensively used as a pigment, and the chromate of oxide of zinc may be used for the same purpose.

A dichromate, composed of one equivalent of chromic acid and two equivalents of protoxide of lead, may be formed by boiling the carbonate of that oxide with excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Mr. Badams as a pigment. (An. of. Phil. xxv. 303.) It may be also made by boiling the neutral chromate with ammonia or lime-water. Liebig and Wöhler prepare it by fusing nitre at a low red heat, and adding chromate of oxide of lead by degrees until the nitre is nearly exhausted. The chromate of potassa and nitre are then removed by water, and the dichromate is left crystalline in texture, and of so beautiful a tint, that it vies with cinnabar. (Pog. An. xxi. 580.)

Bichromate of Chloride of Potassium.—M. Peligot has lately described a crystalline compound in which chloride of potassium acts the part of an alkaline base in relation to chromic acid. It is prepared from bichromate of potassa and concentrated hydrochloric acid in the ratio by weight of about 3 to 4, which are to be boiled together for some time in a rather small quantity of water; and it is deposited in flat quadrangular prisms of the same colour as bichromate of potassa.

In this process there is a mutual interchange between the elements of potassa and hydrochloric acid; such that

2 eq. chromic acid . .	$2(Cr+3O)$	yield	2 eq. chromic acid	$2(Cr+3O)$.
1 eq. potassa . . .	$K+O$		1 eq. chlo. of potassium	$K+Cl$.
1 eq. hydrochloric acid .	$H+Cl$		1 eq. water .	$H+O$.

For this change to ensue there ought to be a certain excess of hydrochloric acid, and yet not so much as to decompose the chromic acid.

This salt should be dried on bibulous paper. It is permanent in the air. In pure water it is decomposed, the materials from which it was formed, bichromate of potassa and hydrochloric acid, being reproduced; but it may be dissolved without such change in water acidulated by hydrochloric acid. M. Peligot has made similar bichromates with the chlorides of sodium, calcium, and magnesium, and with hydrochlorate of ammonia; this last salt being exactly similar in appearance to the bichromate of chloride of potassium. (An. de Ch. et de Ph. lii. 267.)

BORATES.

As the boracic is a feeble acid, it neutralizes alkalies imperfectly; and hence the borates of soda, potassa, and ammonia have always an alkaline reaction. For the same reason, when the borates are digested in any of the more power-

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[*] An. de Ch. et de Ph. vol. xxii. [†] Annals of Philosophy, vol. xvi.

ful acids, such as the sulphuric, nitric, or hydrochloric, the boracic acid is separated from its base. This does not happen, however, at high temperatures; for boracic acid, owing to its fixed nature, decomposes at a red heat all salts, not excepting sulphates, the acid of which is volatile.

The borates of the alkalies are soluble in water, but most of the other salts of this acid are of sparing solubility. They are not decomposed by heat, and the alkaline and earthy borates resist the action of heat and combustible matter. They are remarkably fusible in the fire, a property obviously owing to the great fusibility of boracic acid itself.

The borates are distinguished by the following character:—By digesting any borate in a slight excess of strong sulphuric acid, evaporating to dryness, and boiling the residue in strong alcohol, a solution is formed, which has the property of burning with a green flame. (Page 205.)

Biborate of Soda.—This salt, the only borate of importance, occurs native in some of the lakes of Thibet and Persia, and is extracted from this source by evaporation. It is imported from India in a crude state, under the name of *tincal*, which, after being purified, constitutes the *refined borax* of commerce. It is frequently called *subborate of soda*, a name suggested by the inconsistent and unphilosophical practice, now quite inadmissible, of regulating the nomenclature of salts merely by their action on vegetable colouring matter. It crystallizes in hexahedral prisms, which effloresce on exposure to the air, require twenty parts of cold, and six of boiling water for solution. When exposed to heat the crystals are first deprived of their water of crystallization, and then fused, forming a vitreous transparent substance called *glass of borax.* The crystals are composed of 69.8 parts or two eq. of boracic acid, 31.3 or one eq. of soda, and 90 or ten eq. of water.

The chief use of borax is as a flux, and for the preparation of boracic acid. Biborate of magnesia is a rare natural production, which is known to mineralogists by the name of *boracite.*

A new biborate of soda, which contains half as much water of crystallization as the preceding, has been lately described by M. Buran. It is harder and denser than borax, is not efflorescent, and crystallizes in regular octohedrons. It is made by dissolving borax in boiling water until the specific gravity of the solution is at 30° or 32° of Baumé's hydrometer: the solution is then very slowly cooled; and when the temperature descends to about 133°, the new salt is deposited. It is found to be more convenient for the use of jewellers than common borax. (An. de Ch. et de Ph. xxxvii. 419.)

CARBONATES.

The carbonates are distinguished from other salts by being decomposed with effervescence, owing to the escape of carbonic acid gas, by nearly all the acids; and all of them, except the carbonates of potassa, soda, and lithia, may be deprived of their acid by heat. The carbonates of baryta and strontia, especially the former, require an intense white heat for decomposition; those of lime and magnesia are reduced to the caustic state by a full red heat; and the other carbonates part with their carbonic acid when heated to dull redness.

All the carbonates, except those of potassa, soda, and ammonia, are of sparing solubility in pure water; but all of them are more or less soluble in an excess of carbonic acid, owing doubtless to the formation of supersalts.

The former nomenclature of the salts is peculiarly exceptionable as applied to the carbonates. The two well-known carbonates of potassa, for example, are distinguished by the propositions *sub* and *super*, as if the one had an alkaline, and the other an acid reaction; whereas, in fact, according to their action on test paper, they are both subsalts. I shall adopt the nomenclature which has been employed with other salts, applying the generic name of carbonate to those salts which contain one equivalent of carbonic acid, and one equivalent of the base,—compounds which may be regarded as neutral in composition, however they may act on the colouring matter of plants. The formula for the neutral protocarbonates is $\dot{M}+\ddot{C}$, the acid containing twice as much oxygen as the base.

Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, and the protoxides of manganese, iron, copper, and lead; together with some double carbonates, such as Dolomite, or the double carbonate of lime and magnesia, and barytocalcite, or the double carbonate of baryta and lime.

The composition of the principal carbonates is stated in the following table:

Names.	Base.		Acid.		Equiv.	Formulæ.
Carbonate of potassa .	47.15	1 eq.+	22.12	1 eq.=	69.27	$\dot{K}+\ddot{C}$.
Bicarbonate of potassa .	47.15	1 eq.+	44.24	2 eq.=	91.39	$\dot{K}+2\ddot{C}$.
Do. in crystals with 9 or 1 eq. of water					=100.39	
Carbonate of soda . .	31.3	1 eq.+	22.12	1 eq.=	53.42	$\dot{Na}+\ddot{C}$.
Do. in crystals with 90 or 10 eq. of water					=143.42	
Do. in crystals with 63 or 7 eq. of water					=116.42	
Bicarbonate of soda .	31.3	1 eq.+	44.24	2 eq.=	75.54	$\dot{Na}+2\ddot{C}$.
Do. in crystals with 9 or 1 eq. of water					= 84.54	
Carbonate of ammonia .	17.15	1 eq.+	22.12	1 eq.=	39.27	$H^3N+\ddot{C}$.
Bicarbonate of ammonia	17.15	1 eq.+	44.24	2 eq.=	61.39	$H^3N+2\ddot{C}$.
Carbonate of baryta .	76.7	1 eq.+	22.12	1 eq.=	98.82	$\dot{Ba}+\ddot{C}$.
Carbonate of strontia	51.8	1 eq.+	22.12	1 eq.=	73.92	$\dot{Sr}+\ddot{C}$.
Carbonate of lime (marble)	28.5	1 eq.+	22.12	1 eq.=	50.62	$\dot{Ca}+\ddot{C}$.
Carbonate of magnesia	20.7	1 eq.+	22.12	1 eq.=	42.82	$\dot{Mg}+\ddot{C}$.
Do. in crystals with 27 or 3 eq. of water					= 69.82	
Carbonate protox. of iron	36	1 eq.+	22.12	1 eq.=	58.12	$\dot{Fe}+\ddot{C}$.
Dicarbonate protox. copper	79.2	2 eq.+	22.12	1 eq.=	101.32	$2\dot{Cu}+\ddot{C}$.
Do. in malachite with 9 or 1 eq. of water					=110.32	
Carbonate protox. lead	111.6	1 eq.+	22.12	1 eq.=	133.72	
Dicarb. perox. mercury	436	2 eq.+	22.12	1 eq.=	458.12	$2\ddot{Hg}+\ddot{C}$.

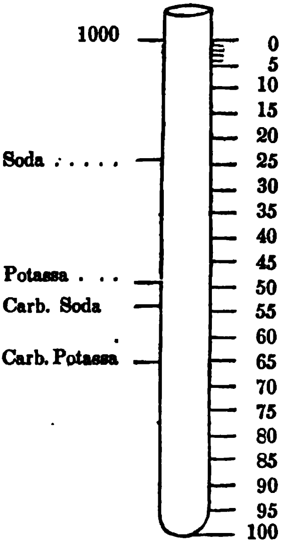
Double Carbonates.

Carbonate of lime and magnesia	Carb. lime . .	50.62	1 eq.	= 93.44	$\dot{Mg}\ddot{C}+\dot{Ca}\ddot{C}$.
	Carb. magnesia	42.82	1 eq.		
Carb. of baryta and lime	Carb. baryta	98.82	1 eq.	=149.44	$\dot{Ca}\ddot{C}+\dot{Ba}\ddot{C}$.
	Carb. lime .	50.62	1 eq.		

Carbonate of Potassa.—This salt is procured in an impure form by burning land plants, lixiviating their ashes, and evaporating the solution to dryness, a process which is performed on a large scale in Russia and America. The carbonate, thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is much employed in the arts especially in the formation of soap and the manufacture of glass. When derived from this source it always contains other compounds, such as sulphate of potassa and chloride of potassium; and, therefore, for chemical purposes, it should be prepared from cream of tartar. On heating this salt to redness, the tartaric acid is decomposed, and a pure carbonate of potassa mixed with charcoal remains. The carbonate is then dissolved in water, and, after filtration, is evaporated to dryness in a capsule of platinum or silver.

Pure carbonate of potassa has a taste strongly alkaline, is slightly caustic, and communicates a green tint to the blue colour of the violet. It dissolves in less than an equal weight of water at 60°, deliquesces rapidly on exposure to the air, and crystallizes with much difficulty from its solution. In pure alcohol it is insoluble. It fuses at a full red heat, but undergoes no other change.

It is often necessary, for commercial purposes, to ascertain the value of different samples of pearlash; that is, to determine the quantity of real carbonate of potassa contained in a given weight of impure carbonate. A convenient mode of effecting this object is described by Mr. Faraday in this excellent work on *Chemical Manipulation*. Into a tube sealed at one end, 9½ inches long, ¾ths of an inch in diameter, and as cylindrical as possible in its whole length, pour 1000 grains of water, and with a file or diamond mark the place where its surface reaches, and divide the space occupied by the water into 100 equal parts, as is shown in the annexed wood-cut. Opposite to the numbers 23.44, 48.96, 54.63, and 65, draw a line, and at the first write soda, at the second potassa, at the third carbonate of soda, and at the fourth carbonate of potassa. Then prepare a dilute acid having the specific gravity of 1.127 at 60°, which may be made by mixing one measure of concentrated sulphuric acid with four measures of distilled water. This is the standard acid to be used in all the experiments, being of such strength that when poured into the tube till it reaches either of the four marks just mentioned, we shall obtain the exact quantity which is necessary for neutralizing 100 grains of the alkali written opposite to it. If, when the acid reaches the word *carb. potassa*, and when, consequently, we have the exact quantity which will neutralize 100 grains of that carbonate, pure water be added until it reaches 0, or the beginning of the scale, each division of this mixture will neutralize one grain of carbonate of potassa. All that is now required, in order to ascertain the quantity of real carbonate in any specimen of pearlash, is to dissolve 100 grains of the sample in warm water, filter to remove all the insoluble parts, and add the dilute acid in successive small quantities, until by the test of litmus paper, the solution is exactly neutralized. Each division of the mixture indicates a grain of pure carbonate. It is convenient, in conducting this process, to set aside a portion of the alkaline liquid, in order to neutralize the acid, in case it should at first be added too freely. To this instrument the term *alkalimeter* is given, a name obviously derived from the use to which it is applied.



Bicarbonate of Potassa is made by transmitting a current of carbonic acid gas through a solution of the carbonate; or by evaporating a mixture of the carbonates of ammonia and potassa, the ammonia being dissipated in a pure state. By slow evaporation, the bicarbonate is deposited from the liquid in hydrated prisms with eight sides, terminated with dihedral summits, the primary form of which is a right rhomboidal prism.

Bicarbonate of potassa, though far milder than the carbonate, is alkaline both to the taste and to test paper. It does not deliquesce on exposure to the air. It requires four times its weight of water at 60° for solution, and is much more soluble at 212°; but it parts with some of its acid at that temperature. At a low red heat it is converted into the carbonate.

Dr. Thomson, in his "First Principles," has described a sesquicarbonate, which was discovered by Dr. Nimmo of Glasgow. Its crystals contain twelve equivalents of water, as denoted by the formula $\dot{K}^2\ddot{C}^3+12\dot{H}$.

Carbonate of Soda.—The carbonate of commerce is obtained by lixiviating the ashes of sea-weeds. The best variety is known by the name of *barilla*, and is derived chiefly from the *salsola soda* and *salicornia herbacea*. A very inferior kind, known by the name of *kelp*, is prepared from sea-weeds on the northern shores of Scotland. The purest barilla, however, though well fitted for making soap and glass, and for other purposes in the arts, always contains the sulphates of potassa and soda, and the chlorides of potassium and sodium. A purer carbonate is prepared by heating a mixture of sulphate of soda, saw-dust, and lime in a reverberatory furnace. By the action of carbonaceous matter, the sulphuric acid is decomposed; its sulphur partly uniting with calcium and partly being dissipated in the form of sulphurous acid, while the carbonic acid, which is generated during the process, unites with soda. The carbonate of soda is then obtained by lixiviation and crystallization. It is difficult to obtain this salt quite free from sulphuric acid.

Carbonate of soda crystallizes in octohedrons with a rhombic base, the acute angles of which are generally truncated. The crystals effloresce on exposure to the air, and when heated dissolve in their water of crystallization. By continued heat they are rendered anhydrous without loss of carbonic acid. They dissolve in about two parts of cold, and in rather less than their weight of boiling water, and the solution has a strong alkaline taste and reaction. The crystals commonly found in commerce contain ten equivalents of water; but when formed at a temperature of about 80°, they retain only seven equivalents.

The purity of different specimens of barilla, or other carbonates of soda, may be ascertained by means of the alkalimeter above described.

Bicarbonate of Soda.—This salt is made by the same processes as bicarbonate of potassa, and is deposited in hydrated crystalline grains by evaporation. Though still alkaline, it is much milder than the carbonate, and far less soluble, requiring about ten times its weight of water at 60° for solution. It is decomposed partially at 212°, and is converted into the carbonate by a red heat.

Sesquicarbonate.—This compound occurs native on the banks of the lakes of soda in the province of Sukena in Africa, whence it is exported under the name of *trona*. It was first distinguished from the two other carbonates by Mr. Phillips, (Journal of Science, vii.) whose analysis corresponds with that of Klaproth. Its formula is $\dot{\mathrm{Na}}^2\ddot{C}^3+4\dot{H}$.

Carbonate of Ammonia.—The only method of procuring this salt is by mixing dry carbonic acid over mercury with twice its volume of ammoniacal gas. It is a dry white volatile powder of an ammoniacal odour, and alkaline reaction.

Bicarbonate of Ammonia.—This salt was formed by Berthollet by transmitting a current of carbonic acid gas through a solution of the common carbonate of ammonia of the shops. On evaporating the liquid by a gentle heat, the bicarbonate is deposited in small six-sided prisms, which have no smell, and very little taste: their primary form, according to Mr. Miller of

Cambridge, is a right rhombic prism. Berthollet ascertained that it contains twice as much acid as the carbonate.

Sesquicarbonate of Ammonia.—The common carbonate of ammonia of the shops, *Sub-carbonas Ammoniæ* of the Pharmacopœia, is different from both these compounds. It is prepared by heating a mixture of one part of hydrochlorate of ammonia with one part and a half of carbonate of lime, carefully dried. Double decomposition ensues during the process: chloride of calcium remains in the retort, and hydrated sesquicarbonate of ammonia is sublimed. The carbonic acid and ammonia are, indeed, in proper proportion in the mixture for forming the real carbonate; but from the heat employed in the sublimation, part of the ammonia is disengaged in a free state.

The salt thus formed consists, according to the analysis of Phillips, Ure, and Thomson, of 34.3 parts or two eq. of ammonia, 66.36 parts or three eq. of carbonic acid, and 18 parts or two eq. of water. When recently prepared, it is hard, compact, translucent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly from the escape of pure ammonia, and becomes an opaque brittle mass, which is the bicarbonate.

Carbonate of Baryta occurs abundantly in the lead mines of the north of England, where it was discovered by Dr. Withering, and has hence received the name of *Witherite.* It may be prepared by way of double decomposition by mixing a soluble salt of baryta with any of the alkaline carbonates or bicarbonates. It is anhydrous, exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60°, and 2300 of boiling water for solution; but when recently precipitated, it is dissolved much more freely by a solution of carbonic acid. It is highly poisonous.

Carbonate of Strontia, which occurs native at Strontian in Argyleshire, and is known by the name of *Strontianite*, may be prepared in the same manner as carbonate of baryta. It is anhydrous, and very insoluble in pure water, but is dissolved by an excess of carbonic acid.

Carbonate of Lime.—This salt is a very abundant natural production, and occurs under a great variety of forms, such as common limestone, chalk, marble, and Iceland spar, and in regular anhydrous crystals, the density of which is 2.7. It may also be formed by precipitation. Though sparingly soluble in pure water, it is dissolved by carbonic acid in excess; and hence the spring-water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

Daniell noticed that an aqueous solution of sugar and lime deposited crystallized carbonate of lime by exposure to the air. Gay-Lussac has proved that the sugar merely acts as a solvent, presenting lime in a favourable state for combining with the carbonic acid of the atmosphere; and that all the lime is deposited in acute rhombohedrons, which contain five eq. of water to one eq. of carbonate of lime. These crystals are insoluble and remain unchanged in cold water; but in water at 86°, or in air, they lose their combined water, and fall to powder. When boiled in alcohol they retain their form, but lose two eq. of water and retain three eq. in combination. (An. de Ch. et de Ph. xlviii. 301.)

Carbonate of Magnesia.—It is met with occasionally in small acicular crystals, and in a pulverulent earthy state, but more commonly as a compact mineral of an earthy fracture called *magnesite.* A specimen of magnesite from the East Indies, where I am informed it is abundant, has been analyzed by Dr. Henry, who found it to be nearly pure anhydrous carbonate of magnesia: it is of a snow-white colour, of density 2.56, and so hard that it strikes fire with steel. (An. of Phil. xvii. 252.) It is obtained in minute transparent hexagonal prisms with three eq. of water, when a solution of bicarbonate of magnesia evaporates spontaneously in an open vessel. The crystals lose their water and become opaque by a very gentle heat, and even in a dry air at 60°. By cold water they are decomposed, yielding a soluble bicarbonate and an insoluble white compound of hydrate and carbonate of magnesia; and hot water produces the same change with disengagement of carbonic acid, without dissolving any magnesia. (Berzelius.)

When carbonate of potassa is added in excess to a hot solution of sulphate of magnesia, a white precipitate falls, which after being well washed has been long considered as pure carbonate of magnesia; but Berzelius has shown that it consists of the following ingredients:

Magnesia .	44.75	82.8 or 4 eq.	Probable formula is $\dot{Mg}\dot{H}^4+3\dot{Mg}\ddot{C}$.
Carbonic acid .	35.77	66.36 or 3 eq.	
Water . .	19.48	36 or 4 eq.	
	100.00	185.16 or 1 eq.	

This compound is said to require 2493 parts of cold, and 9000 of hot water for solution. It is freely dissolved by a solution of carbonic acid, bicarbonate of magnesia being generated; but on allowing the solution to evaporate spontaneously, carbonic acid is given off, and crystals of the hydrated carbonate above mentioned are obtained.

Carbonate of Protoxide of Iron.—Carbonic acid does not form a definite compound with peroxide of iron, but with the protoxide it constitutes a salt which is an abundant natural production, occurring sometimes massive, and at other times crystallized in rhombohedrons or hexagonal prisms. This protocarbonate is contained also in most of the chalybeate mineral waters, being held in solution by free carbonic acid; and it may be formed by mixing an alkaline carbonate with the sulphate of protoxide of iron. When prepared by precipitation, it attracts oxygen rapidly from the atmosphere, and the protoxide of iron, passing into the state of peroxide, parts with carbonic acid. For this reason, the carbonate of iron of the Pharmacopœia is of a red colour, and consists chiefly of the peroxide.

Dicarbonate of Protoxide of Copper.—It occurs as a hydrate in the beautiful green mineral called *malachite;* and the same compound, as a green powder, the *mineral green* of painters, may be obtained by precipitation from a hot solution of sulphate of protoxide of copper by carbonate of soda or potassa. When obtained from a cold solution, it falls as a bulky hydrate of greenish-blue colour, which contains more water than the green precipitate. By careful drying its water may be expelled. When the hydrate is boiled for a long time in water it loses both carbonic acid and combined water, and the colour changes to brown. The rust of copper, prepared by exposing metallic copper to air and moisture, is a hydrated dicarbonate.

The blue-coloured mineral, called *blue copper ore*, appears to be a hydrate and carbonate of the protoxide of copper, and consists, according to the analysis of Mr. Phillips, of (Quarterly Journal of Science, iv.)

Protoxide of copper	69.08	118.8 3 eq.	Probable formula is $\dot{Cu}\dot{H}+2\dot{Cu}\ddot{C}$.
Carbonic acid .	25.46	44.24 2 eq.	
Water . .	5.46	9 1 eq.	
	100.00	171.24 1 eq.	

The blue pigment called *verditer*, prepared by decomposing nitrate of oxide of copper with chalk, has a similar composition. (Phillips.)

Carbonate of Protoxide of Lead.—This salt, which is the *white lead* or *ceruse* of painters, occurs native in white prismatic crystals derived from a right rhombic prism, the sp. gravity of which is 6.72. It is obtained as a white pulverulent precipitate by mixing solutions of an alkaline carbonate with acetate of protoxide of lead; and it is prepared as an article of commerce from the subacetate by a current of carbonic acid, by exposing metallic lead in minute division to air and moisture, and by the action on thin sheets of lead of the vapour of vinegar, by which the metal is both oxidized and converted into a carbonate.

Dicarbonate of Peroxide of Mercury.—When a solution of the nitrate of peroxide of mercury is decomposed by carbonate of soda, an ochre-yellow precipitate falls, which Mr. Phillips finds to be a dicarbonate. The protoxide appears to form no compound with carbonic acid; for when a nitrate of that oxide is decomposed by any alkaline carbonate, the precipitate is either black at first or speedily becomes so, and after being washed is quite free from carbonic acid.

Double Carbonates.—One of the most remarkable of these is the double carbonate of lime and magnesia, which constitutes the minerals called bitter-spar, pearl-spar, and Dolomite. The two former occur in rhombohedrons of nearly the same dimensions as carbonate of lime. The latter is met with in great perfection in the Alps, and there usually occurs in white masses of a granular texture: the grains often cohere loosely, but other specimens are hard and compact, and when broken present the crystalline aspect of marble. Its density is 2.884. Some specimens consist of the two constituent carbonates in the ratio of their equivalents, as stated in the table; but the ratio of the ingredients, as may be expected, is very variable, since isomorphous substances crystallize together in all proportions. Carbonate of protoxide of manganese is often associated with them. The rock called *magnesian limestone* may be viewed as an impure earthy variety of Dolomite.

The double carbonate of baryta and lime constitutes the mineral called *barito-calcite*, which Mr. Children found to contain the two carbonates in atomic proportion.

Berthier has made some interesting experiments on the production of double carbonates by fusion. Carbonate of soda, when fused with carbonate of baryta, strontia, or lime, in the ratio of their equivalents, yields uniform crystalline compounds, which have all the appearance of being definite. An equivalent of Dolomite fuses in like manner with four equivalents of carbonate of soda. Five parts of carbonate of potassa and four of carbonate of soda, corresponding to an equivalent of each, fuse with remarkable facility; and this mixture, by reason of its fusibility, may be advantageously employed in the analysis of earthy minerals.

Compounds similar to the foregoing may be generated by heating sulphate of soda with carbonate of baryta, strontia, or lime, in the ratio of their equivalents: or by employing the sulphate of these bases and carbonate of soda. In like manner carbonate of soda fuses with chloride of barium or calcium; and chloride of sodium with carbonate of baryta or lime. (An. de Ch. et de Ph. xxxviii. 246

SECTION II.

CLASS OF SALTS. ORDER II.

HYDRO-SALTS.

In this section are included those salts only, the acid or base of which is a compound containing hydrogen as one of its elements. For reasons already assigned (page 291) I have already described all those salts which were formerly called *muriates* or *hydrochlorates* of metallic oxides as chlorides of metals, considering that in general the neutralizing power of hydrochloric acid is not due to its direct combination with an oxide, but to chlorine uniting with the metal itself. The same remark applies to the hydriodic and other hydracids, the salts of which are consequently reduced to a small number. The only salts, indeed, which are included in this section, are compounds of the hydracids with ammonia and phosphuretted hydrogen. Some of the compounds which might, as containing an hydracid, be comprehended in this section, may with greater propriety be placed in the fourth, seeing that in them the hydracid acts rather as a base or electro-positive ingredient than as an acid or electro-negative substance. This double function, which chemists have long recognized in certain metallic oxides, such as alumina and oxide of zinc, appears to be performed even by so powerful an acid as the hydrochloric. Some judicious observations on this subject have been made by Professor Kane of Dublin. (Dublin Journal of Science, i. 265.)

Ammonia unites with fluoride of boron, bisulphuret of carbon, and some other bi-elementary compounds, which contain neither oxygen nor hydrogen, constituting saline combinations, which are included in this section, and to which, considering the distinct alkaline character of ammonia, the ordinary nomenclature of salts is applicable.

AMMONIACAL SALTS.

These compounds, like the oxy-salts of ammonia, are readily recognized by the addition of pure potassa or lime, when the odour of ammonia may be perceived. Those which contain a volatile acid may in general be sublimed without decomposition; but the ammonia is expelled by heat from those acids which are much more fixed than itself. The most important of these salts are thus constituted:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Hydrochlorate of ammonia	17.15 1 eq. +	36.42 1 eq. =	53.57	$H^{3}N + HCl$.
Hydriodate do. . .	17.15 1 eq. +	127.3 1 eq. =	144.45	$H^{3}N + HI$.
Hydrobromate do. .	17.15 1 eq. +	79.4 1 eq. =	96.55	$H^{3}N + HBr$.
Hydrofluate do. . .	17.15 1 eq. +	19.68 1 eq. =	36.83	$H^{3}N + HF$.
Hydrosulphate do. .	17.15 1 eq. +	17.1 1 eq. =	34.25	$H^{3}N + HS$.
Hydrocyanate do. . .	17.15 1 eq. +	27.39 1 eq. =	44.54	$H^{3}N + HC^{2}N$.
Hydrosulphocyanate do.	17.15 1 eq. +	59.59 1 eq. =	76.74	$H^{3}N + HCyS^{2}$.
Trifluoborate do. . .	51.45 3 eq. +	66.94 1 eq. =	118.39	$3H^{3}N + BF^{3}$.
Difluoborate do. . .	34.3 2 eq. +	66.94 1 eq. =	101.24	$2H^{3}N + BF^{3}$.
Fluoborate do. . . .	17.15 1 eq. +	66.94 1 eq. =	84.09	$H^{3}N + BF^{3}$.
Fluosilicate do. . . .	17.15 1 eq. +	26.18 1 eq. =	43.33	$H^{3}N + SiF$.
Carbosulphate do. . .	17.15 1 eq. +	38.32 1 eq. =	55.47	$H^{3}N + CS^{2}$.

Hydrochlorate of Ammonia.—This salt, *sal ammoniac* of commerce, was formerly imported from Egypt, where it is procured by sublimation from the soot of camel's dung; but it is now manufactured in Europe by several processes. The most usual is to decompose sulphate of ammonia by the chloride either of sodium or magnesium, when double decomposition ensues, giving rise in both cases to hydrochlorate of ammonia, and to sulphate of soda when chloride of sodium is used, and to sulphate of magnesia when chloride of magnesium is employed. The sal ammoniac is afterwards obtained in a pure state by sublimation. The method now generally used in this country for obtaining sulphate of ammonia is to decompose with sulphuric acid the hydrosulphate and hydrocyanate of ammonia which is collected in the manufacture of coal-gas; but it may also be procured either by lixiviating the soot of coal, which contains sulphate of ammonia in considerable quantity, or by digesting with gypsum impure carbonate of ammonia, procured from the destructive distillation of bones and other animal substances, so as to form an insoluble carbonate of lime and a soluble sulphate of ammonia.

Hydrochlorate of ammonia has a pungent saline taste, has a density of 1.45, and is tough and difficult to be pulverized. It is soluble in alcohol and water, requiring for solution three times its weight of water at 60°, and an equal weight at 212°. It usually crystallizes from its solution in feathery crystals, but sometimes in cubes or octohedrons. At a temperature below that of ignition it sublimes without fusion or decomposition, and condenses on cool surfaces as an anhydrous salt, which absorbs humidity in a damp atmosphere, but is not deliquescent. It is generated by the direct union of hydrochloric acid and ammoniacal gases, which unite in equal volumes.

Hydriodate of Ammonia.—It is formed as a white powder by the direct union in equal measures of hydriodic acid and ammoniacal gases, or by neutralizing a solution of hydriodic acid with ammonia, and evaporating. It crystallizes with difficulty in anhydrous cubes, is very soluble in water, and deliquesces in a moist atmosphere. In close vessels it may be sublimed without change; but suffers partial decomposition when heated in the open air.

When a concentrated solution of this salt is digested with iodine, a brown solution is obtained, the nature of which is not understood.

Hydrobromate of Ammonia is a white anhydrous salt which may be formed by similar processes as the hydriodate. It is soluble in water, and crystallizes by evaporation in quadrilateral prisms.

Hydrofluate of Ammonia.—It is prepared by mixing 1 part of sal ammoniac with 2¼ of fluoride of sodium, both dry and in fine powder, gently heating the mixture in a platinum vessel, and receiving the sublimed salt in a second platinum vessel, the temperature of which is not allowed to exceed 212°. Chloride of sodium is generated, and hydrofluate of ammonia is obtained in small anhydrous prismatic crystals, which may be preserved unchanged in the air, is partly soluble in alcohol, and dissolves readily in water. At an elevated temperature it fuses before subliming. It acts powerfully on glass even in its dry state.

When this salt is introduced in a dry state into ammoniacal gas, absorption ensues, and the resulting salt appears to be a dihydrofluate of ammonia. By sublimation it loses ammonia and becomes neutral. An acid salt, apparently a bihydrofluate, is obtained by evaporating the aqueous solution of the neutral hydrofluate, ammonia being disengaged. If the evaporation take place at 100°, it separates in crystalline grains, which redden litmus, and deliquesce rapidly at common temperatures.

Hydrosulphate of Ammonia.—This salt, also called hydrosulphuret of ammonia, and formerly the *fuming liquor of Boyle*, is prepared by heating a mixture of one part of sulphur, two of sal ammoniac, and two of unslaked lime. The changes which ensue have been explained by Gay-Lussac. The volatile products are ammonia and hydrosulphate of ammonia; and the fixed residue consists of sulphate of lime with chloride and sulphuret of calcium. The hydrosulphuric acid is formed from the hydrogen of hydrochloric acid uniting with sulphur, and the oxygen of the sulphuric acid is derived from decomposed lime, the calcium of which is divided between the chlorine of the hydrochloric acid and sulphur. Hydrosulphate of ammonia may also be formed by the direct union of its constituent gases, and if they are mixed in a glass globe kept cool by ice, the salt is deposited in crystals. It is much used as a reagent, and for this purpose is usually prepared by saturating a solution of ammonia with hydrosulphuric acid gas.

Hydrocyanate of Ammonia.—This salt is a constant product of the destructive distillation of animal substances, and may be obtained in a pure state by saturating hydrocyanic acid with ammonia. It is extremely volatile, and crystallizes when condensed in cubic crystals. It is very liable to spontaneous decomposition, when it becomes black, from the separation of a carbonaceous mass which retains nitrogen.

Sulphocyanate of Ammonia is prepared by neutralizing hydrosulphocyanic acid with ammonia, or heating a mixture of dry sulphocyanuret of potassium and sal ammoniac. It is very soluble, deliquesces in the air, and crystallizes with difficulty.

Fluoborates of Ammonia.—Fluoboric acid combines with three times and with twice its volume of ammoniacal gas, forming a trifluoborate and difluoborate, which are liquid at common temperatures. The neutral fluoborate is formed of equal volumes of its constituent gases, and is a white volatile salt, soluble in water, but which cannot be recovered from the solution; for on evaporation, a subfluoborate of ammonia is expelled, and boracic acid is left in solution. The neutral fluoborate is formed by heating gently either of the subfluoborates.

Fluosilicate of Ammonia.—Fluosilicic acid and ammoniacal gases unite by volume in the ratio of 1 to 2, forming a white volatile salt which is decomposed by water.

Carbosulphate of Ammonia.—When dry ammoniacal gas is brought into contact with bisulphuret of carbon, direct combination ensues, and there results an uncrystalline solid mass of a straw-yellow colour, which may be sublimed without decomposition. By contact with water, or exposure to a moist air, an interchange ensues between the elements of water and bisulphuret of carbon, giving rise to hydrosulphuric and carbonic acids; and a sulphur-salt of an orange-yellow colour, the hydrocarbosulphuret of ammonia,* is generated.

Arsenio-persulphate of Ammonia.—Berzelius states that when dry persulphuret of arsenic is exposed to ammoniacal gas, absorption ensues, and a yellowish-white compound results; but the elements are united by a feeble attraction, and on mere exposure to the air, the ammonia escapes.

SALTS OF PHOSPHURETTED HYDROGEN.

Rose has lately called the attention of chemists to the close analogy which exists in the composition of ammonia and phosphuretted hydrogen, and in some of their properties. The latter is a feeble alkaline base, which combines with some of the hydracids. The salt best known is the hydriodate of phosphuretted hydrogen, first noticed by Gay-Lussac, which is formed of 127.3 parts or one eq. of acid and 34.4 parts or one eq. of base, and crystallizes in cubes. The crystals are permanent while quite dry; but with water, or the moisture of the air, they yield a solution of hydriodic acid, and phosphuretted hydrogen gas escapes. These salts are all decomposed by water, and exist only in the anhydrous state.

SECTION III.

CLASS OF SALTS. ORDER III.

SULPHUR-SALTS.

THE compounds described in this section are double sulphurets, just as the oxy-salts in general are double oxides. Their resemblance in composition to salts is perfect. The principal *sulphur-bases* are the protosulphurets of potassium, sodium, lithium, barium, strontium, calcium, and magnesium, and hydrosulphate of ammonia; and the principal *sulphur-acids* are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold, together with hydrosulphuric acid, hydrosulphocyanic acid, bisulphuret of carbon, and sulphuret of selenium. The sulphur-salts with two metals are so constituted, that if the sulphur in each were replaced by an equivalent quantity of oxygen, an oxy-salt would result. The analogy between oxy-salts and sulphur-salts is rendered still closer by the circumstance that hydrosulphuric and hydrosulphocyanic acids have the characteristic properties of acidity, and unite both with ammonia and with sulphur-bases.

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* It is not very clear what combination Dr. Turner intends by the name, *hydro-carbosulphuret of ammonia;* but it is probable that he means to designate the sulphur-salt called further on, *carbo-sulphuret of hydrosulphate of ammonia. See page* 473.—*Ed.*

The sulphur-salts may be divided into families, characterized by containing the same sulphur-acid. For the purpose of indicating that such salts are double sulphurets, as well as to distinguish them readily from other kinds of salts, I shall construct the generic name of each family from the sulphur-acid terminated with sulphuret. Thus the salts which contain persulphuret of arsenic or hydrosulphuric acid as the sulphur-acid are termed *arsenio-sulphurets* and *hydro-sulphurets;* and a salt composed of each of these sulphur-acids with sulphuret of potassium is termed *arsenio-sulphuret* and *hydro-sulphuret* of sulphuret of potassium. For the sake of brevity the metal of the base may alone be expressed, it being understood that the positive metal in a sulphur-salt enters as a protosulphuret into the compound.*

HYDRO-SULPHURETS.

The sulphur-salts contained in this group have hydro-sulphuric acid for their electro-negative ingredient. Most of them which have been studied are soluble in water, and may be obtained in crystals by evaporation. They are decomposed by exposure to the air, yielding at first bisulphurets of the metal, and then a hyposulphite. By acids the hydrosulphuric acid is expelled with effervescence. They are thus constituted:—

Name.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Hydrosulphuret of potassium . .	55.25 1 eq.	+ 17.1 1 eq.	= 72.35	$KS + HS$.
Ditto sodium .	39.4 1 eq.	+ 17.1 1 eq.	= 56.5	$NaS + HS$.
Ditto lithium .	26.1 1 eq.	+ 17.1 1 eq.	= 43.2	$LS + HS$.
Ditto barium .	84.8 1 eq.	+ 17.1 1 eq.	= 101.9	$BaS + HS$.
Ditto strontium .	59.9 1 eq.	+ 17.1 1 eq.	= 77.	$SrS + HS$.
Ditto calcium .	36.6 1 eq.	+ 17.1 1 eq.	= 53.7	$CaS + HS$.
Ditto magnesium	28.8 1 eq.	+ 17.1 1 eq.	= 45.9	$MgS + HS$.

Hydro-sulphuret of Potassium.—This salt is obtained in the anhydrous state by introducing anhydrous carbonate of potassa into a tubulated retort, transmitting through it a current of hydrosulphuric acid gas, and heating the salt to low redness. The mass becomes black, fuses, and boils from the escape of carbonic acid gas and aqueous vapour; and after the ebullition has ceased, the gas is continued to be transmitted, until the retort is quite cold. The resulting anhydrous hydro-sulphuret of potassium, though black while in fusion, is white when cold, and of a crystalline texture; but if air had not been perfectly excluded, it has a yellow tint, owing to the presence of some bisulphuret of potassium.

The same salt is prepared in the moist way by introducing a solution of pure potassa, free from carbonic acid, into a tubulated retort, expelling atmospheric air by a current of hydrogen gas, and then saturating the solution with hydrosulphuric acid. At first the potassa, as in the former process, interchanges elements with the gas, yielding water and protosulphuret of potassium; after which the protosulphuret unites with hydrosulphuric acid. The solution should be evaporated in the retort to the consistence of syrup, a current of hydrogen gas being transmitted through the apparatus the whole time; and on cooling the salt crystallizes in large four or six-sided prisms, which are colourless if air was perfectly excluded. The crystals contain water of crystallization, have an acrid, alkaline, and bitter taste, deliquesce in open vessels, and dissolve freely in water and alcohol. On exposure to the air it acquires a yellow colour, from the formation of bisulphuret of potassium.

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* Dr. Hare has adopted an ingenious plan for naming the sulphur-salts, founded on the nomenclature of the oxy-salts. Considering the electro-negative sulphuret in the sulphur-salts as performing the part of an acid, he calls it an acid, and forms its name by changing the termination of the element with which the sulphur is combined into ic, and prefixing *sulph* or *sulpho.* Thus, taking the examples given by Dr. Turner, he calls persulphuret of arsenic, *sulpharsenic acid,* and its sulphur-salts, *sulpharseniates;* while he denominates hydrosulphuric acid, *sulphydric acid,* and its salts *sulphydrates.* In indicating the sulphur-base, Dr. Hare has adopted the same plan which Dr. Turner recommends in the text, of expressing the metal only of the sulphur-base, the metal being understood to be in the state of protosulphuret.—*Ed.*

Hydro-sulphuret of Sodium.—It is prepared on the same principles as the former salt, and yields by evaporation colourless crystals. When a hot concentrated solution is mixed with a solution of hydrate of soda also concentrated, the mixture on cooling deposites four-sided prisms, which are protosulphuret of sodium with water of crystallization. The interchange of elements is such that

1 eq. hydro-sulphuret and 1 eq. soda yield 2 eq sulphuret and 1 eq. water.

$$(Na+S)+(H+S) \quad Na+O \quad \text{yield} \quad 2(Na+S) \quad H+O.$$

Hydro-sulphuret of Lithium may be prepared in the same way as the two former salts, and is left by evaporation as a crystalline solid. When heated in close vessels it parts with its water of crystallization, and like the two former salts retains its acid even at a red heat.

Hydro-sulphuret of Barium.—It is prepared by the action of hydrosulphuric acid on a solution of baryta with the precautions already mentioned for excluding atmospheric air, and crystallizes by evaporation in four-sided prisms, which are very soluble in water, but dissolve sparingly in alcohol. The crystals part with their water of crystallization when heated, and at a commencing red heat give out hydrosulphuric acid, leaving pure sulphuret of barium.

Hydro-sulphuret of Strontium is prepared like the former salt, and crystallizes in large radiated prisms, which when quite dry may be kept several days exposed to the air without change. When heated it loses its water and acid, and protosulphuret of strontium as a white powder is left.

Hydro-sulphuret of Calcium is formed in the same manner as the preceding salts; but it exists only in solution; for on attempting to crystallize by evaporation, hydrosulphuric acid is driven off, and the sulphuret of calcium in prisms of a silky lustre is deposited. The hydro-sulphuret of magnesium likewise exists only in solution.

HYDRO-SULPHOCYANURETS.

The acid of these salts is hydrosulphocyanic acid. The only ones yet known are those of sulphuret of potassium and hydrosulphate of ammonia, which are thus constituted:—

Names.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Hydro-sulphocyan. of potassium	55.25 1 eq. +	59.59 1 eq. =	114.84	$KS+HCyS^2$.
Hydro-sulphocyan. of hydrosulphate of ammonia	34.25 1 eq. +	59.59 1 eq. =	93.84	$(H^3N+HS)+HCyS^2$.

Hydro-sulphocyanuret of Potassium.—Zeise prepares this salt by decomposing with pure potassa the corresponding ammoniacal salt, and evaporating in vacuo along with sulphuric acid, which unites both with its water and free ammonia. The residue is a white crystalline salt, soluble both in water and alcohol.

Hydro-sulphocyanuret of Hydrosulphate of Ammonia.—It is prepared, according to Zeise, by saturating with ammoniacal gas 100 measures of alcohol at a temperature of 50°, diluting with 50 measures of alcohol, and adding 16 measures of bisulphuret of carbon. In about half an hour a deposite of carbo-sulphuret of hydrosulphate of ammonia ensues, which is separated by filtration through linen, and the clear liquor is received in a flask, tightly corked, and exposed for 10 hours to a temperature of 60°. It is then exposed for 24 hours to a cold of 32°, during which the hydro-sulphocyanuret separates in long brilliant crystals of a lemon-yellow colour. The crystals are first washed with cold alcohol and then with ether, and dried on bibulous paper, and in vacuo. They may be preserved in a dry state, but decompose readily when moist, and are very soluble in water.

CARBO-SULPHURETS.

The acid of these sulphur-salts is bisulphuret of carbon; and the salts themselves are thus constituted:—

Names.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Carbo-sulphuret of potassium	55.25 1 eq. +	38.32 1 eq. =	93.57	$KS+CS^2$.
Ditto sodium	39.4 1 eq. +	38.32 1 eq. =	77.72	$NaS+CS^2$.
Ditto lithium	26.1 1 eq. +	38.32 1 eq. =	64.42	$LS+CS^2$.
Ditto hydrosulphate of ammonia	34.25 1 eq. +	38.32 1 eq. =	72.57	$(H^3N+HS)+CS^2$.
Ditto barium	84.8 1 eq. +	38.32 1 eq. =	123.12	$BaS+CS^2$.
Ditto strontium	59.9 1 eq. +	38.32 1 eq. =	98.22	$SrS+CS^2$.
Ditto calcium	36.6 1 eq. +	38.32 1 eq. =	74.92	$CaS+SC^2$.
Ditto magnesium	28.8 1 eq. +	38.32 1 eq. =	67.12	$MgS+CS^2$.

Carbo-sulphuret of Potassium.—On agitating bisulphuret of carbon with a strong alcoholic solution of protosulphuret of potassium, the liquid when set at rest separates into three layers, the lowest of which is carbo-sulphuret of potassium, and is of the consistence of syrup. Another process is to digest bisulphuret of carbon at 86° in a corked bottle full of a strong aqueous solution of protosulphuret of potassium, until the latter is saturated. A concentrated solution of this salt is of a deep orange, almost red, colour; and when evaporated at 86° to the consistence of syrup, a deliquescent yellow crystalline salt is deposited, which is sparingly soluble in alcohol. On heating it to 150° it gives off water of crystallization; and when more strongly heated it is resolved into tersulphuret of potassium and charcoal.

Carbo-sulphuret of Sodium.—It is prepared like the former salt, and separates in yellow crystals from a very concentrated solution. It is deliquescent, and dissolves readily in alcohol as well as water.

Carbo-sulphuret of Lithium resembles the preceding salt, and is very soluble in water and alcohol.

Carbo-sulphuret of Hydrosulphate of Ammonia.—Zeise prepares this salt by filling a bottle with ten measures of nearly absolute alcohol saturated with ammoniacal gas and one measure of bisulphuret of carbon, and inserting a tight cork. As soon as the liquid has acquired a yellowish-brown colour, the bottle is plunged into ice-cold water, when the carbo-sulphuret is deposited either in yellow penniform crystals or as a crystalline powder. The whole is thrown upon a linen filter, and the salt after being washed, first with absolute alcohol and then with ether, is dried by pressure within folds of bibulous paper. This salt is very volatile, passing off entirely at common temperatures, and can only be preserved in well-corked bottles. Exposed to the air it absorbs humidity and acquires a red colour. Its solution may be kept unchanged in bottles filled with it and tightly corked.

The carbo-sulphurets of barium, strontium, and calcium, may be obtained by acting on bisulphuret of carbon with a solution of the protosulphurets of those metals. The resulting solutions are of an orange or brown colour, and the salts deposited by evaporation are of a citron-yellow when quite dry, The carbo-sulphuret of barium is of sparing solubility. The carbo-sulphuret of magnesium is best prepared by adding sulphate of magnesia to a solution of carbo-sulphuret of barium. Berzelius has also prepared several carbo-sulphurets of the metals of the second class.

ARSENIO-SULPHURETS.

Berzelius finds that each of the three sulphurets of arsenic (page 358) is capable of acting as a sulphur-acid, giving rise to three distinct families of sulphur-salts, distinguishable by the terms *arsenio-persulphurets*, *arsenio-sesquisulphurets*, and *arsenio-protosulphurets.*

Persulphuret of arsenic is a very powerful sulphur-acid, violently displacing hydrosulphuric acid from its combinations with sulphur-bases, even at common temperatures; and when digested with earthy or alkaline carbonates, it expels carbonic acid. The salts of this sulphur-acid may be prepared by several methods:—

1. By digesting the persulphuret of arsenic in a solution of a sulphur-base, such as a sulphuret of potassium or sodium, until it is saturated. The resulting soluble arsenio-persulphuret may be employed to prepare insoluble salts of the same sulphur-acid by means of double decomposition. If a persulphuret of potassium is used, sulphur is deposited.

2. By decomposing a hydrosulphuret of a sulphur-base with persulphuret of arsenic, in which case hydrosulphuric gas is disengaged with effervescence.

3. By decomposing a solution of an arseniate by means of hydrosulphuric acid or hydrosulphate of ammonia.

4. By dissolving persulphuret of arsenic in a solution of caustic alkali, such as potassa; when an interchange of elements between portions of the alkali and persulphuret ensues, whereby arsenic acid and protosulphuret of potassium are generated. In this case

1 eq. persulphuret & 5 eq. potassa yield 1 eq. arsenic acid & 5 eq. protosulphuret.
$2\,As+5S$ $5(K+O)$ $2\,As+5O$ $5(K+S)$.

Two salts are thus generated and co-exist in the solution, namely, arseniate of potassa and arsenio-persulphuret of potassium. Similar changes invariably occur when sesquisulphuret of arsenic, sesquisulphuret of antimony, and other sulphur-acids are boiled with alkaline solutions: an oxy-salt, the acid of which is formed of oxygen and the electro-negative metal, is always generated; and this salt, if soluble in water, remains together with the sulphur-salt in solution. An alkaline carbonate may be substituted for a pure alkali, but then carbonic acid is expelled. These principles are concerned in the production of kermes, as already explained (page 378).

5. The last method which requires mention, is by exposing a mixture of persulphuret of arsenic and an alkaline carbonate to a red heat in a covered vessel. Carbonic acid gas is disengaged; and an interchange of elements, similar to that just explained, takes place between a portion of the alkali and the sulphuret. The fused mass, accordingly, contains an arseniate of the alkali, as well as sulphur-salt. This tendency to the formation of a double sulphuret is the reason why, in decomposing orpiment by black flux, the whole of the arsenic is never sublimed; a part is uniformly retained in the form of a sulphur-salt, the arsenio-sesquisulphuret of sulphuret of potassium.

Most of the arsenio-persulphurets of the second class of metals are insoluble; but those of the metals of the alkalies and alkaline earths are very soluble in water, have a lemon-yellow colour in the anhydrous state, and are colourless when combined with water of crystallization or in solution. When exposed to heat in close vessels they give off sulphur, and an arsenio-sesquisulphuret is generated. In the solid state they are very permanent in the air, and even in solution oxidation takes place with great slowness. When decomposed by an acid, persulphuret of arsenic subsides, hydrosulphuric acid gas escapes, and a salt of the alkali is generated. Some chemists may doubt the possibility of the arsenio-persulphurets dissolving as such in water: they may consider the arsenic, and the metal of the sulphur-base to be united with oxygen, and all the sulphur with hydrogen; but this supposition, if followed out, leads into such complex and improbable modes of combination, that I see no alternative but implicitly to admit the views here adopted.

The following table exhibits the composition of the principal arsenio-persulphurets:—

Names.	Sulph.-base.	Sulph.-acid.	Equiv.	Formulæ.
Triarsenio-persulph. of potassium	165.75 3 eq.	+155.9 1 eq.	=321.65	$3KS+As^2S^5$.
Diarsenio-persulph. do.	110.5 2 eq.	+155.9 1 eq.	=266.4	$2KS+As^2S^5$.
Arsenio-persulph. do.	55.25 1 eq.	+155.9 1 eq.	=211.15	$KS+As^2S^5$.
Triarsenio-persulph. of sodium .	118.2 3 eq.	+155.9 1 eq.	=274.1	$3NaS+As^2S^5$.
Do. in crystals with 270 or 30 eq. of water			=544.1	
Diarsenio-persulph. do.	78.8 2 eq.	+155.9 1 eq.	=234.7	$2NaS+As^2S^5$.
Arsenio-persulph. do.	39.4 1 eq.	+155.9 1 eq.	=195.3	$NaS+As^2S^5$.
Triarsenio-persulph. of hydrosulphate of ammonia	102.75 3 eq.1	+55.9 1 eq.	=258.65	$3(H^3N+HS)$ $+As\ S^5$.
Diarsenio-persulph. do.	68.5 2 eq	+155.9 1 eq.	=224·4	$2(H^3N+HS)$ $+As^2S^5$.
Arsenio-persulph. do.	34.25 1 eq.	+155.9 1 eq.	=190.15	(H^3N+HS) $+As^2S^5$.

Arsenio-persulphurets of Potassium.—The diarsenio-persulphuret is best obtained by the action of hydrosulphuric acid gas on the diarseniate of potassa, and yields a colourless solution. By evaporation in vacuo it is reduced to a yellowish viscid mass which dries imperfectly, but, when exposed for some time to the open air, at length becomes a crystalline mass of a lemon-yellow colour, in which rhomboidal tables are perceptible. When this salt is mixed with alcohol, it is resolved into the triarsenio-persulphuret, which is insoluble in the alcohol, and the arsenio-persulphuret, which remains in solution. The latter has not been obtained in the solid state. The former is deliquescent and very soluble in water: but when its solution is gently evaporated, the residue has a radiated crystalline texture.

Arsenio-persulphurets of Sodium.—The diarsenio-persulphuret is formed like the corresponding salt of potassium, is very soluble in water, and by evaporation yields a lemon-yellow mass, which attracts humidity from the air. On mixing its solution with alcohol it is resolved into the arsenio-persulphuret and triarsenio-persulphuret of sodium, and the latter falls in scaly crystals of snowy whiteness, which may be collected on a filter, washed with alcohol, and dried without change. This salt by solution in water and evaporation may be obtained in rhomboidal tables or prisms derived from a rhombic prism. The crystals undergo no change in the air, and contain thirty equivalents of water. The arsenio-persulphuret has been obtained only in solution. The *arsenio-persulphurets of lithium* are very analogous to those of sodium.

Arsenio-persulphurets of hydrosulphate of Ammonia.—The diarsenio-persulphuret is obtained as a colourless solution by decomposing with hydrosulphuric acid gas a solution of diarseniate of ammonia. By spontaneous evaporation it becomes a viscid mass of a reddish-yellow colour, and which cannot be fully dried without decomposition. When its solution is mixed with hydresulphate of ammonia and agitated with hot alcohol, the triarsenio-sulphuret is deposited in colourless prisms, which, after being well washed with alcohol and dried on bibulous paper, undergo no change by exposure to the air. The arsenio-persulphuret remains in the alcoholic solution.

Analogous salts may be similarly prepared with barium, strontium, cium, and magnesium; and insoluble compounds of the same nature may be formed by way of double decomposition by mixing soluble arsenio-persulphurets with oxy-salts of the second class of metals.

The salts in which sesquisulphuret of arsenic acts as an acid, resemble those of the persulphuret both in their general characters and mode of formation. Those formed with the protosulphuret of arsenic cannot be made in the moist way by direct union of their ingredients; but when solutions of the arsenio-sesquisulphurets are evaporated, spontaneous decomposition takes place, the salts of protosulphuret of arsenic of a reddish-brown colour subside, while arsenio-persulphurets remain in solution.

MOLYBDO-SULPHURETS.

The electro-negative ingredient of these salts is the tersulphuret of molybdenum, and the most remarkable of them is the molybdo-sulphuret of potassium, which is readily formed by decomposing with hydrosulphuric acid gas a rather strong solution of molybdate of potassa. If no iron is present, the liquid acquires a beautiful red colour like the solution of bichromate of potassa, and on evaporation prismatic crystals with four and eight sides are deposited. Berzelius describes this compound as one of the most beautiful which chemistry can produce: the crystals, by transmitted light, are ruby-red, and their surfaces, while moist with the solution which yielded them, shine like the wings of certain insects with a metallic lustre of a rich green tint. The crystals are anhydrous, dissolve readily in water, but are insoluble in alcohol. On the addition of sulphuric or any of the stronger acids, a salt of potassa is generated with escape of hydrosulphuric acid, and precipitation of tersulphuret of molybdenum.

Soluble molybdo-sulphurets of sodium, lithium, and hydrosulphate of ammonia of a red colour, may be obtained by a process similar to that for preparing the preceding compound. The composition of these salts is as follows:—

Names.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Molybdo-sulphuret of potassium	55.25	1 eq. + 96	1 eq. = 151.25	$KS + MoS^3$
Molybdo-sulphuret of sodium	39.4	1 eq. + 96	1 eq. = 135.4	$NaS + MoS^3$
Molybdo-sulphuret of lithium	26.1	1 eq. + 96	1 eq. = 122.1	$LS + MoS^3$
Molybdo-sulphuret of hydrosulphate of ammonia	34.25	1 eq. + 96	1 eq. = 130.25	$(H^3N + HS) + MoS^3$

Similarly constituted soluble salts of a red or orange colour may be obtained by boiling solutions of sulphuret of barium, strontium, and calcium with an excess of tersulphuret of molybdenum. The insoluble molybdo-sulphurets may be prepared from the former by way of double decomposition.

ANTIMONIO-SULPHURETS.

When two parts of carbonate of potassa are intimately mixed with four of sesquisulphuret of antimony and one part of sulphur, and the mixture is fused, an antimonio-persulphuret of potassium is generated. On digesting in water, a subantimonio-persulphuret is dissolved, and is deposited by gentle evaporation in large colourless tetrahedrons, which become yellow on exposure to the air. The salts which this sulphur-acid forms with other bases have not been examined.

A sulphur-salt of potassium, in which sesquisulphuret of antimony is the acid, remains in solution after the kermes is deposited (379), and may be obtained by evaporation in vacuo in colourless irregular crystals which deliquesce rapidly in the air.

TUNGSTO-SULPHURETS.

The best known of these salts is that of potassium, in which tersulphuret of tungsten is combined with protosulphuret of potassium. It is formed when a solution of tungstate of potassa is decomposed by hydrosulphuric acid, and crystallizes by evaporation in flat quadrilateral prisms, which are anhydrous, and are of a pale red colour. It dissolves sparingly in alcohol, but is freely soluble in water, yielding an orange-coloured solution. When mixed with a quantity of acid insufficient for entire decomposition, it forms a bitungsto-sulphuret of a brown colour.

The tungsto-sulphuret of potassium unites with tungstate of potassa as a double salt, which yields a yellow solution, and crystallizes in rectangular tables of a lemon-yellow colour. It combines also with nitrate of potassa, and the resulting double salt crystallizes in large transparent crystals of a ruby-red tint, and when heated detonates like gunpowder.

The tungsto-sulphuret of sodium is prepared from tungstate of soda by hydrosulphuric acid, and crystallizes with difficulty in irregular crystals of a red colour. It deliquesces in the air, and is soluble in water and alcohol.

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SECTION IV.

CLASS OF SALTS. ORDER IV.

HALOID SALTS.

In this section are included substances composed like the preceding salts of two bi-elementary compounds, one or both of which are analogous in composition to sea-salt. The principal groups consist of double chlorides, double iodides, double fluorides, and double cyanurets. In these the haloid-bases belong usually to the electro-positive metals, and the haloid-acids to the metals which are electro-negative. I shall apply to them the same principle of nomenclature as to the sulphur-salts.*

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* Dr. Hare has adopted for these compounds the same plan of nomenclature as for the sulphur-salts.—See note, page 471. Viewing, as Dr. Turner has done, the double haloid salts of Berzelius as simple salts, consisting of two bi-elementary compounds, the more electro-negative compound acting the part of an acid, the other of a base, he has applied to the former the generic appellation of acid, and named the salts themselves on the same plan as the oxy-salts. Accordingly, he has given the usual acid termination to the name of the more electro-positive element of the compound acting as the acid, considering this element as the radical, and prefixes to it syllables indicating the other element. Where oxygen is the electro-negative element of an acid, it is understood to be present, without any syllables being prefixed to indicate its presence; but where other elements replace oxygen in compounds having the nature of ordinary acids, it is obviously necessary to indicate the replacing element. Adopting these principles of nomenclature, Dr. Hare has chlorohydrargyrates, chloroaurates, iodoplatinates, bromohydrargyrates, fluohydrates, fluoborates, fluosilicates, cyanoferrates, &c., corresponding with Dr. Turner's hydrargo-chlorides, auro-chlorides, platino-iodides, hydrargo-bromides, hydro-fluorides, boro-fluorides, silico-fluorides, and ferro-cyanurets, &c.—*Ed.*

HYDRARGO-CHLORIDES.

The haloid-acid of this family is bichloride of mercury, which reddens litmus paper, and loses the property when a haloid-base is present, thus bearing a close analogy to ordinary acids. Its principal salts which have been examined are thus constituted:—

Names.	Basic chloride.	Bichlor. Merc.	Equiv.	Formulæ.
Dihydrargo-chloride of potassium	149.14 2 eq.	+ 272.84' 1 eq.	= 421.98	$2KCl + HgCl^2$.
Do. in rhombic prisms with 18 or 2 eq. of water			= 439.98	
Hydrargo-chloride of potassium	74.57 1 eq.	+ 272.84 1 eq.	= 347.41	$KCl + HgCl^2$.
Do. in acicular crystals with 18 or 2 eq. of water			= 365.41	
Bihydrargo-chloride of potassium	74.57 1 eq.	+ 545.68 2 eq.	= 620.25	$KCl + 2HgCl^2$.
Do. in acicular crystals with 36 or 4 eq. of water			= 656.25	
Hydrargo-chloride of sodium	58.72 1 eq.	+ 272.84 1 eq.	= 331.56	$NaCl + HgCl^2$.
Do. in crystals with 36 or 4 eq. of water			= 367.56	
Dihydrargo-chloride of hydrochlorate of ammonia.	107.14 2 eq.	+ 272.84 1 eq.	= 379.98	$2(H^3N + HCl) + HgCl^2$.
Do. in flat rhombic prisms with 18 or 2 eq. of water			= 397.98.	

The preceding salts, except the last, were first prepared and examined by Bonsdorff (An. de Ch. et de Ph. xliv. 189); and they are obtained by mixing the ingredients in the ratio for combining, and setting aside the solution to crystallize. The ammoniacal salt has long been known under the name of *salt of alembroth*. Bonsdorff obtained similar compounds with the chlorides of lithium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. Those of lithium, calcium, magnesium, and zinc are deliquescent. The hydrargo-chlorides of iron and manganese are isomorphous, and crystallizes in rhombic prisms. Hydrochloric acid combines with b chloride of mercury, and yields a very soluble salt, which may be obtained in crystals: the electro-positive ingredient is here probably hydrochloric acid, and as such will be considered as chloride of hydrogen, with properties analogous to the chlorides of electro-positive metals.

AURO-CHLORIDES.

These salts, the electro-negative ingredient of which is the terchloride of gold, have been studied by Berzelius, Johnston, and Bonsdorff. They are prepared by mixing the chlorides in atomic proportions, and setting aside the solution to crystallize.

Most of them have an orange or yellow colour, and consist of single equivalents of their constituent chlorides, as is exemplified by the composition of the three following salts:—

Names.	Basic chloride.	Terch. Gold.	Equiv.	Formulæ.
Auro-chloride of potassium	74.57 1 eq.	+ 305.46 1 eq.	= 380.03	$KCl + AuCl^3$.
Do. in prisms with 45 or 5 eq. of water			= 425.03	
Auro-chloride of sodium	58.72 1 eq.	+ 305.46 1 eq.	= 364.18	$NaCl + AuCl^3$.
Do. in 4-sided pr. with 36 or 4 eq. of water			= 400.18	

Names.	Basic chloride.	Terch. Gold.	Equiv.	Formulæ.
Auro-chloride of hydrochlorate of ammonia	53.57 1 eq.+	305.46 1 eq.=	359.03	(H^3N+HCl) $AuCl^3$.
Do. in acicular crystals with 36 or 4 eq. of water			=395.03	

Auro-chloride of Potassium.—This salt crystallizes either in striated prisms or thin hexagonal tables, which effloresce in a dry air, and lose all their water at 212°. At a red heat the terchloride of gold is decomposed, leaving chloride of potassium and metallic gold. This salt is soluble both in water and alcohol.

Auro-chloride of Sodium crystallizes in long quadrilateral prisms, which may be exposed to the air without change, and fuse readily in their water of crystallization. The *auro-chloride of lithium* is deliquescent.

Auro-chloride of Hydrochlorate of Ammonia.—It crystallizes in transparent needles or small prisms, which become opaque by exposure to the air, and are soluble in water and alcohol.

Auro-chloride of Hydrogen.—In this compound hydrochloric acid is probably the positive chloride. It crystallizes readily in long acicular crystals of a light yellow colour when an acid solution of gold is cautiously evaporated. The crystals undergo no change in dry air, but in a moist atmosphere deliquesce into a yellow liquid.

Bornsdorff has prepared the auro-chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. Most of them crystallize in prisms and contain water of crystallization.

PLATINO-CHLORIDES.

Both the protochloride and bichloride of platinum act as haloid-acids. Magnus prepared the *platino-protochloride of potassium* by mixing chloride of potassium with a solution of protochloride of platinum in hydrochloric acid. It crystallizes by evaporation in red, anhydrous, 4-sided prisms, which are insoluble in alcohol, but dissolve readily in water. It consists of single equivalents of its constituent chlorides.

The *platino-protochloride of sodium* may also be prepared, is soluble in water and alcohol, and crystallizes with difficulty. A similar salt may be formed with hydrochlorate of ammonia, and is isomorphous with that of potassium, which it also resembles in its properties, composition, and mode of preparation.

The solution of protochloride of platinum in hydrochloric acid, which has a deep red tint, is doubtless a double chloride, but it has not been obtained in crystals.

The principal salts of bichloride of platinum are those of potassium, sodium, and hydrochlorate of ammonia, which are thus constituted:—

Names.	Basic chloride.	Bichl. of Plat.	Equiv.	Formulæ.
Platino-bichloride of potassium	74.57 1 eq.+	169.64 1 eq.=	244.21	$KCl+PlCl^2$.
Platino-bichloride of sodium	58.72 1 eq.+	169.64 1 eq.=	228.36	$NaCl+PlCl^2$.
Do. in prisms with 54 or 6 eq. of water			=282.36	
Platino-bichloride of hydrochlorate of ammonia	53.57 1 eq.+	169.64 1 eq.=	223.21	(H^3N+HCl) $+PlCl^2$.

Platino-bichloride of Potassium.—The production of this salt by mixing its constituents in solution, constitutes one of the best tests for potassa (page 297.) It is commonly obtained as a powder of a pale lemon-yellow colour; but by slow evaporation it yields small octohedrons of a brilliant lustre. It is anhydrous, insoluble in alcohol, and is sparingly dissolved by cold, but more freely by hot water. Heated to redness it yields chlorine, and the residue consists of platinum and chloride of potassium.

Platino-bichloride of Sodium.—This salt crystallizes in fine transparent prisms of a deep yellow colour, which are soluble in water and alcohol. When gently heated it loses its water of crystallization, and becomes a pale yellow powder.

Platino-bichloride of Hydrochlorate of Ammonia falls as a lemon-yellow powder when sal ammoniac is mixed with a strong solution of bichloride of platinum. It resembles the double salt of potassium in its properties and form, crystallizing in small anhydrous octohedrons when its aqueous solution is slowly evaporated. This salt is employed in the preparation of platinum, and when heated to redness leaves that metal in a spongy state.

Bonsdorff has prepared the platino-bichlorides of barium, strontium, calcium, and several other metals. Most of them crystallize with water of crystallization, and have a yellow or orange colour.

PALLADIO-CHLORIDES.

Both of the chlorides of palladium act as haloid-acids, combining with many of the metallic chlorides, when their respective solutions are mixed and evaporated. The principal palladio-chlorides which have been examined are those with the chlorides of potassium and sodium, and with hydrochlorate of ammonia, which consist of single equivalents of their ingredients.

The palladio-protochloride of potassium crystallizes in four-sided prisms of a dirty yellow colour, which are anhydrous, insoluble in alcohol, and freely soluble in water. The corresponding salt of sodium is deliquescent and soluble both in water and alcohol. That of hydrochlorate of ammonia is isomorphous with the salt of potassium, which it resembles in its other properties.

The palladio-bichloride of potassium is obtained by evaporating the palladio-protochloride with nitro-hydrochloric acid, when microscopic crystals of a cinnabar-red colour are deposited, which by a glass are found to be regular octohedrons. It is anhydrous, insoluble in alcohol, and nearly so in water. When heated, or by continued ebullition, it is reconverted into the palladio-protochloride of potassium. The corresponding salt of hydrochlorate of ammonia is obtained in a similar manner, and resembles the former in form and other properties.

RHODIO-CHLORIDES.

The sesquichloride of rhodium combines with the chlorides of potassium and sodium, and the resulting salts are thus constituted:—

Names.	Basic Chlor.	Sesquichl. Rhod.	Equiv.	Formulæ.
Dirhodio-chloride of potassium	149.14 2 eq.	+ 210.66 1 eq.	= 39.58	$2KCl + R^2Cl^3$.
Do. in four-sided prisms with 18 or 2 eq. of water			= 377.8	
Trirhodio-chloride of sodium	176.16 3 eq.	+ 210.66 1 eq.	= 386.82	$3NaCl + R^2Cl^3$.
Do. in prisms with 162 or 18 eq of water			= 548.82	

Dirhodio-chloride of Potassium.—It is obtained by mixing the respective chlorides in the ratio above assigned, and crystallizes in four-sided rectangular prisms, which are of a deep red colour, insoluble in alcohol, and contain 18 parts or two eq. of water combined with 359.8 parts or one eq. of the salt.

Hydrochlorate of ammonia yields a similar double salt, analogous in its properties to the preceding.

Trirhodio-chloride of Sodium.—This salt crystallizes in large prismatic crystals of a deep red colour, which lose part of their water in a dry air, and become covered with a red powder. They are insoluble in alcohol.

IRIDIO-CHLORIDES.

The chlorides of iridium act as haloid-acids. The most remarkable of its salts is the iridio-bichloride of potassium, which in form and properties resembles the platino-bichloride of potassium, crystallizing in brilliant octohedrons, but of a black colour, which are sparingly soluble in water. Hydrochlorate of ammonia forms with it a similar salt, which is of a deep cherry-red colour.

OSMIO-CHLORIDES.

Berzelius has described the osmio-bichloride of potassium, which resembles in form, composition, and most of its properties the corresponding salts of platinum and iridium. It is insoluble in alcohol, and but sparingly dissolved in water; but its aqueous solution, when gently evaporated, yields octohedron crystals of a deep brown colour.

OXY-CHLORIDES.

Chemists are acquainted with a considerable number of compounds in which a metallic oxide is united with a chloride either of the same metal, which is the most frequent, or of some other metal. These compounds are commonly termed *sub-muriates*, on the supposition that they consist of hydrochloric acid combined with two or more equivalents of an oxide.

Oxy-chlorides of Iron.—When the crystallized protochloride of iron is heated without exposure to the air, the last portions of its water exchange elements with part of the chloride of iron, yielding hydrochloric acid, which is evolved, and protoxide of iron. On raising the heat so as to expel the pure chloride of iron, a deep green oxy-chloride in scaly crystals remains. (Berzelius.)

The ochreous matter which falls when a solution of the protochloride of iron is exposed to the air, is hydrated peroxide of iron combined with some perchloride. A similar hydrate is obtained by mixing with a solution of the perchloride of iron a quantity of alkali insufficient for complete decomposition. When a solution of the perchloride is evaporated to dryness without exposure to the air, the last portions of water exchange elements with the perchloride, hydrochloric acid is disengaged, and after subliming the pure anhydrous perchloride, a compound in large, brown, shining laminæ is left, which consists of peroxide and perchloride of iron. (Berzelius.)

Mr. Phillips has described a soluble oxy-chloride, which appears to consist of one eq. of perchloride of iron with nine eq. of the peroxide. It is prepared by digesting hydrochloric acid with the required proportion of the moist hydrated peroxide. The solution is of a brownish-red colour, and a precipitate is occasioned either by a little more of the peroxide or a little acid, indicating the formation of other oxy-chlorides which are insoluble. (Phil. Mag. and An. viii. 406.)

Oxy-chlorides of Tin.—When a large quantity of water is poured on crystallized protochloride of tin, a portion of water and protochloride exchange elements, an acid solution is formed, containing the double chloride of tin and hydrogen, and a white powder subsides, which is a compound of the protoxide and protochloride of tin.

Oxy-chloride of Antimony.—It falls as a white curdy precipitate when sesquichloride of antimony is thrown into water (page 377); and according to an analysis by Phillips contains about 7.8 per cent. of chlorine.

Oxy-chloride of Cerium.—This compound is generated by heating the hydrated protochloride, just as when the protochloride of iron is distilled.

Oxy-chloride of Bismuth.—It is prepared by pouring a neutral solution of nitrate of oxide of bismuth into a concentrated solution of sea-salt; and a similar compound, but with more oxide, is formed when a dilute solution of sea-salt is used. They are both heavy insoluble powders of a very white colour.

Oxy-chloride of Copper.—This compound falls as a green hydrate when potassa is added to a solution of chloride of copper insufficient for its complete decomposition. When its water is expelled it becomes of a liver-brown colour. Berzelius states it to consist of one eq. of the chloride and three eq. of oxide of copper. It is used as a pigment under the name of *Brunswick green*, being prepared for that purpose by exposing metallic copper to hydrochloric acid or a solution of sal ammoniac. The same compound is generated during the corrosion of copper in sea-water.

Oxy-chlorides of Lead.—A compound of one eq. protochloride to two eq. of protoxide of lead has been found as a colourless mineral. Another oxychloride with three eq. of the protoxide is prepared by adding pure ammonia to a hot solution of chloride of lead. It falls as a heavy white hydrate; but on expelling its water by heat, it acquires a pale yellow colour. A third oxy-chloride with a still larger proportion of oxide is used as a pigment under the name of *mineral* or *patent yellow;* and it is prepared by the action of moist sea-salt on litharge, by which means portions of the protoxide and sea-salt exchange elements, yielding soda and chloride of lead. After washing away the alkali, the mixed oxide and chloride are dried and fused.

Oxy-chloride of Mercury.—This compound is obtained as a shining crystalline powder, of a brownish-black colour, when peroxide of mercury is boiled with a solution of the bichloride. It is anhydrous, and consists of single equivalents of the oxide and chloride.

CHLORIDES WITH AMMONIA.

Several interesting compounds of chlorides with ammonia have been studied by Persoz and Rose. (An. de Ch. et de Ph. xliv. 315, and li. 5, and Pog. Annalen, xx. 149.) The perchlorides of chromium, tin, titanium, antimony, and iron absorb ammonia at common temperatures; and most of the other chlorides absorb it when gently warmed. The chlorides of potassium, sodium, and barium do not absorb ammonia, while those of strontium and calcium combine with four equivalents of the alkali. Chloride of copper absorbs three equivalents, and acquires the same deep blue tint as the ammoniaco-sulphate of copper. Chloride of nickel unites with three, and chloride of cobalt with two equivalents of ammonia. Chloride of silver takes up slowly one and a half equivalents. Calomel absorbs half an equivalent and forms a black compound; but on exposure to the air, the ammonia flies off, and pure white calomel remains. Corrosive sublimate, by the aid of heat, rapidly absorbs half an equivalent of ammonia, and forms a white compound, which is insoluble in water, and bears a considerable temperature without decomposition: the white precipitate of pharmacy is probably analogous in nature, though the ratio of its ingredients is different. Perchloride of titanium combines with two equivalents, and that of tin with one. The bromides and iodides, as well as the bicyanuret of mercury, absorb ammonia in the same manner as the chlorides. Nearly all of these compounds depend on very feeble affinities. Most of them lose their ammonia by mere exposure to the air, and it is expelled from nearly all by a very moderate heat; in some, as with perchloride of titanium, heat occasions reactions between the chlorine and ammonia, and the metal is insulated; but in general the alkali is simply expelled, and the chloride returns to its former condition. Though these ammoniacal chlorides may be viewed as salts in which a metallic chloride acts as an acid, they appear to be more closely allied to those singular compounds of ammonia with the oxy-salts which have already been noticed (page 442). To this remark, some of them, of which the ammoniacal chloride of mercury is an instance, are probably exceptions.

CHLORIDES WITH PHOSPHURETTED HYDROGEN.

The analogy which Rose has traced between ammonia and phosphuretted hydrogen is especially remarkable in the compounds which they both form with metallic chlorides. He has examined the compounds of phosphuretted hydrogen with the perchlorides of titanium, tin, antimony, iron and aluminium, all of which correspond to ammoniacal chlorides of similar composition. The phosphuretted hydrogen is in all readily displaced by water, or a solution of ammonia. Rose observed that the resulting chloride is the same in character and composition, whichever of the two kinds of phosphuretted hydrogen were used in its preparation. He also found that the gas, when displaced from perchloride of titanium by water, does not inflame spontaneously; whereas, if displaced by a solution of potassa or its carbonate, by carbonate of ammonia or hydrochloric acid, the gas is spontaneously imflammable. He was thus able to disengage at will either variety of phosphuretted hydrogen from the same compound, without reference to the kind which had been used in its preparation. These facts first led Rose to the opinion that the two gases of phosphorus and hydrogen must be similar in composition. (Page 264.)

DOUBLE IODIDES.

These compounds have not yet been closely studied; but there is no doubt that the iodides are capable of forming with each other an extensive series of compounds. Bonsdorff obtained the hydrargo-biniodide of potassium by saturating a strong solution of iodide of potassium with biniodide of mercury: it may also be formed by dissolving corrosive sublimate in a solution of iodide of potassium, evaporating to dryness, and digesting in alcohol, when the double iodide is dissolved, and chloride of potassium is left. A variety of double iodides have been described by Boullay, and among them a compound of biniodide of mercury and hydriodic acid. (An. de Ch. et de Ph. xxxiv.) In general the double hydrargo-biniodides contain single equivalents of the respective iodides. Liebig obtained a compound of the bichloride and biniodide of mercury, consisting of two eq. of the former to one eq. of the latter, as indicated by the formula $HgI^2+2HgCl^2$.

Several compounds of biniodide of platinum with other iodides have been studied by Mr. Kane of Dublin, and Lassaigne. (Dublin Journal of Science, i. 304, and An. de Ch. et de Ph. li. 125.) The compounds at present known are thus constituted:—

Names.	Basic Iodide.	Biniod. Plat.	Equiv.	Formulæ.
Platino-biniodide of potassium	165.45 1 eq.+	351.4 1 eq.=	516.85	$KI+PlI^2$.
Do. of sodium .	149.6 1 eq.+	351.4 1 eq.=	501	$NaI+PlI^2$.
Do. of hydriodate of ammonia	144.45 1 eq.+	351.4 1 eq.=	495.85	$(H^3N+HI)+PlI^2$.
Do. of barium .	195 1 eq.+	351.4 1 eq.=	546.4	$BaI+PlI^2$.
Do. of zinc .	158.6 1 eq.+	351.4 1 eq.=	510	$ZnI+PlI^2$.
Do. of hydrogen	127.3 1 eq.+	351.4 1 eq.=	478.7	$HI+PlI^2$.

The platino-biniodide of potassium is prepared by digesting an excess of biniodide of platinum in a rather concentrated solution of iodide of potassium. By spontaneous evaporation it crystallizes in small rectangular plates surmounted sometimes with a four-sided pyramid, which are anhydrous, unchanged in the air, and insoluble in alcohol. The colour of the crystals is black with a metallic lustre, and they yield a deep claret-coloured solution with water. The biniodide of platinum appears to combine also with the iodide of platinum; but the compound has only been obtained in solution.

The platino-biniodides of sodium, barium, and zinc, are obtained in the same manner as that of potassium, crystallize with difficulty, are deliquescent in the air, and dissolve in water and alcohol. The ammoniacal salt is analogous in its properties to that of potassium, with which it appears also to be isomorphous.

Platino-biniodide of Hydrogen.—This compound consists of hydriodic acid and biniodide of platinum, in which the former is regarded as the electro-positive element. It is prepared by acting on biniodide of platinum with a cold dilute solution of hydriodic acid, which gradually acquires a deep claret colour, and by evaporation under a bell-jar with quicklime, deposites black acicular crystals. The crystals become moist by exposure to the air.

Oxy-iodides.—The principal oxy-iodides at present known to chemists are those formed by the oxide and iodide of lead. When iodide of potassium is mixed with acetate of oxide of lead in excess, the yellow iodide at first formed combines with oxide of lead and acquires a white colour; and the same compound is obtained directly by employing a subacetate. M. Denot finds that there are three oxy-iodides, in which one eq. of iodide of lead is united with one, two, and five equivalents of oxide of lead.

DOUBLE BROMIDES.

These compounds have not yet been studied; but Bonsdorff has proved the possibility of forming compounds similar in composition and properties to the double chlorides. He obtained the hydrargo-bibromide of potassium in crystals, consisting of an equivalent of each bromide united with two eq. of water.

DOUBLE FLUORIDES.

The researches of Berzelius have led to the formation of several extensive families of double fluorides, in which the fluorides of boron, silicium, titanium, and of other electro-negative metals are the acids, and the fluorides of electro-positive metals are bases. In some instances hydrofluoric acid is a haloid-acid; but more commonly it acts the part of a base.

Hydro-fluorides.—In this family hydrofluoric acid is combined with the fluorides of electro-positive metals. If an equivalent of any electro-positive metal be indicated by M, then the general formula for this family is $MF+HF$.

The hydro-fluoride of potassium is made by mixing hydrofluoric acid with a solution of fluoride of potassium, and evaporating by a gentle heat in a platinum capsule. It commonly crystallizes in confused laminæ; but, by slow evaporation, in square tables or cubes, which are anhydrous and dissolve freely in pure water. It fuses readily when heated, and loses all its hydrofluoric acid at a low red heat.

The hydro-fluoride of sodium is prepared as the preceding salt, and by spontaneous evaporation yields anhydrous rhombohedral crystals. It is sparingly soluble in cold, but much more freely in hot water. The hydro-fluoride of lithium is also of sparing solubility. The fluorides of barium, strontium, calcium, and magnesium, do not combine with hydrofluoric acid.

BORO-FLUORIDES.

When the terfluoride of boron (fluoboric acid gas) is acted upon by water, one out of every four equivalents of the gas interchanges elements with water, giving rise to hydrofluoric and boracic acids, the former of which combines as a haloid-base with undecomposed terfluoride of boron, constituting the boro-hydrofluoric acid (page 241), but which may be viewed as the *boro-fluoride of hydrogen.* This change is such that

$$\begin{array}{llcll}\text{4 eq. terfluoride of boron} & 4(B+3F) & & \text{3 eq. terfluoride of boron} & 3(B+3F)\\ & & \text{yield} & \text{3 eq. hydrofluoric acid} & 3(H+F)\\ \text{and 3 eq. of water} & 3(H+O) & & \text{and 1 eq. boracic acid} & B+3O.\end{array}$$

By careful concentration and cooling, the boracic acid separates as a crystalline powder, and the boro-fluoride of hydrogen remains in solution. It is strongly acid to test paper, and its composition is indicated by the formula

$HF+BF^3$, being an equivalent of each fluoride. On adding potassa to this compound, it interchanges elements with hydrofluoric acid, and there results the boro-fluoride of potassium, $KF+BF^3$, the hydrogen being simply displaced by potassium. The protoxides of most other metals act precisely like potassa, and, therefore, the general formula of these compounds is $MF+BF^3$. When exposed to a strong heat, they all give off terfluoride of boron, and a metallic fluoride is left.

Boro-fluoride of Potassium.—It is prepared by dropping boro-fluoride of hydrogen drop by drop into a solution of a salt of potassa, and falls as a gelatinous transparent hydrate, which is a white very fine powder when dried. It has a slightly bitter taste, and is quite neutral to test paper, is very sparingly soluble in alcohol and cold water, but is dissolved freely by hot water, and subsides on cooling in small brilliant anhydrous crystals. At a strong red heat it gives off the terfluoride of boron and fluoride of potassium remains.

The *boro-fluoride of sodium* is very soluble in water, and is, therefore, best obtained pure by the direct action of boro-fluoride of hydrogen on fluoride of sodium. It crystallizes by slow evaporation in large rectangular prisms, which redden litmus paper strongly. The *boro-fluoride of lithium* also crystallizes in large prisms, is very soluble in water, and deliquesces in the air.

The *boro-fluoride of barium* is prepared by adding carbonate of baryta to boro-fluoride of hydrogen till it ceases to be dissolved, avoiding any further addition. On evaporating to the consistence of a syrup, long acicular crystals form, and by keeping the solution in a warm place, it yields flat, four-sided, rectangular prisms. It is acid to test paper, and deliquescent. The boro-fluorides of calcium and magnesium may be prepared in a similar manner, and are soluble in water. Lead forms a soluble boro-fluoride, which crystallizes in the same manner as the boro-fluoride of barium.

SILICO-FLUORIDES.

The acid solution, called *silico-hydrofluoric acid* (page 327,) may be viewed as the *silico-fluoride of hydrogen*, a compound of 52.36 parts or two eq. of fluoride of silicium and 19.68 or one eq. of fluoride of hydrogen (hydrofluoric acid), as indicated by the formula $HF+2SiF$. When the solution is neutralized with potassa, the alkali interchanges elements with fluoride of hydrogen, water and fluoride of potassium are generated, and the latter combines with the fluoride of silicium. This double fluoride consists, therefore, of 52.36 parts or two eq. of fluoride of silicium, and 57.83 or one eq. of fluoride of potassium, the formula of which is $KF+2SiF$. A similar change ensues with the protoxides of most other metals, and hence the general formula of the silico-fluorides is $MF+2SiF$. On exposing these compounds to a red heat, fluoride of silicium is disengaged.

Silico-fluoride of Potassium.—This salt falls as a very transparent jelly, which has the property of reflecting the colours of the rainbow; but when collected on a filter and dried, it becomes a white powder. By evaporating a saturated aqueous solution, it separates in minute anhydrous crystals. It is sparingly soluble in hot water, and still less so in cold water.

The *silico-fluoride of sodium* resembles the former salt, but is much more soluble in hot water. By evaporation it is obtained in minute anhydrous hexagonal prisms. The silico-fluoride of lithium forms similar crystals, but is more soluble in water.

The *silico-fluoride of barium* gradually falls in microscopic crystals, which through a glass appear as elongated prisms, when chloride of barium is mixed with the silico-fluoride of hydrogen, hydrochloric acid remaining in solution. This salt is very sparingly soluble in water whether hot or cold.

The silico-fluorides of strontium, calcium, magnesium, and lead are best prepared by dissolving their respective carbonates in silico-fluoride of hydrogen. The salt of strontium crystallizes in short quadrilateral prisms, which lose their water of crystallization at a gentle heat and become opaque. For complete solubility in water, they require a slight excess of hydrofluoric acid to be present, and then they dissolve freely. The salt of calcium crystallizes in regular quadrilateral prisms. It dissolves readily in water acidulated with hydrofluoric or hydrochloric acid, but is decomposed by pure water, yielding an acid soluble salt, and an insoluble subsalt. The salts of magnesium and lead are very soluble, and leave a gummy mass by evaporation.

The silico-fluorides of manganese, iron, zinc, cobalt, nickel, and copper are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous, which contain respectively one eq. of fluoride of silicium and seven eq. of water of crystallization.

TITANO-FLUORIDES.

Hydrofluoric acid dissolves titanic acid, and forms with it an acid solution which may be viewed as the titano-fluoride of hydrogen, consisting of 61.66 parts or one eq. of bifluoride of titanium, and 19.68 or one eq. of fluoride of hydrogen, expressed by the formula $HF+TiF^2$. When mixed with potassa, water and fluoride of potassium are generated, and the titano-fluoride of potassium results, the formula of which is $KF+TiF^2$. By substituting most other protoxides for potassa, similar salts may be prepared, the general formula being $MF+TiF^2$.

Few of the titano-fluorides have as yet been studied. That of potassium crystallizes by evaporation in scales like boracic acid, which are anhydrous, and but sparingly soluble in cold water. The titano-fluoride of sodium is very soluble, and crystallizes with difficulty.

Similar double fluorides may be formed, in which the fluorides of molybdenum, tellurium, and platinum, act as the electro-negative ingredients. Few of them, however, have as yet been studied. Berzelius has prepared the alumino-fluorides of potassium and sodium, and the zircono-fluoride of potassium. He employed the latter in the preparation of metallic zirconium. The alumino-fluoride of sodium is found in nature as a rare mineral called *cryolite.*

OXY-FLUORIDES.

Several fluorides combine with oxides in the same manner as chlorides and iodides. An oxy-fluoride of aluminium is prepared as an insoluble gelatinous hydrate by digesting hydrate of alumina in a solution of the sesquifluoride of aluminium. This oxy-fluoride, combined with silicate of alumina, constitutes the topaz. The neutral fluorides of cobalt, nickel, and copper are decomposed by hot water, being resolved into soluble hydro-fluorides, and insoluble oxy-fluorides. Several other fluorides doubtless undergo a similar change. The oxy-fluoride of lead is generated either by digesting fluoride of lead in solution of ammonia, or by fusing together the fluoride and oxide of lead. It is more soluble than the fluoride, and the solution by exposure to the air gives a precipitate of carbonate of oxide of lead. The fluoride of lead also combines by fusion with chloride of lead. Fluoride of calcium forms a very fusible compound with sulphate of lime.

DOUBLE CYANURETS.—FERRO-CYANURETS.

The double cyanurets constitute an extensive and important group of salts, of which a few species only have as yet been studied. Those at present observed by chemists are the ferro-cyanurets, ferro-sesquicyanurets, zinco-cyanurets, cobalto-cyanurets, nicco-cyanurets, and cupro-cyanurets, in which the proto-cyanuret of iron, sesqui-cyanuret of iron, cyanuret of zinc, cyanuret of cobalt, cyanuret of nickel, and cyanuret of copper, may be considered as the electro-negative cyanurets.

Most of the ferro-cyanurets are disalts, in which one equivalent of protocyanuret of iron, FeCy, is combined with two equivalents of some other cyanuret. The general formula of such compounds is $2MCy+FeCy$, in which M represents any electro-positive metal. The elements are in such a ratio, that if the metals were converted into protoxides at the expense of water, the hydrogen would just suffice to form hydrocyanic acid with the cyanogen:—thus would

1 eq. ferro-cyan. $2MCy+FeCy$ yield 2 eq. hydrocy. oxide of M. $2(\dot{M}+HCy)$
and 3 eq. water $3(H+O)$ 1 eq. hydrocy. oxide of iron $\dot{F}e+HCy$.

The ferro-cyanurets in solution may hence be regarded as hydrocyanates of protoxides. But it is better to abstain from such views; for if adopted with one family, they may with equal reason be applied to others, and be extended to the haloid and sulphur-salts generally, which would create much confusion, and a necessity for conceiving very improbable, not to say unchemical, modes of combination.

The ferro-cyanurets of the metals of the alkalies and alkaline earths are soluble in water: those of the metals of the earths have not been prepared at all; and those of the second class of metals are insoluble. The latter may readily be obtained from the former by means of double decomposition. When the soluble ferro-cyanurets are dried and heated to redness in close vessels, the electro-positive cyanuret escapes decomposition, while the negative cyanuret is resolved into carburet of iron and nitrogen, the latter escaping as gas. The insoluble ferro-cyanurets undergo complete decomposition by heat, either nitrogen gas, or nitrogen mixed with cyanogen gas being evolved. The iron in solutions of the soluble ferro-cyanurets is not detected by alkalies, or hydrosulphuric acid. When acted on by the stronger acids, such as the sulphuric, the electro-positive cyanuret is resolved by decomposition of water into hydrocyanic acid and an oxide of the metal; while a white precipitate falls, principally containing cyanuret of iron, which yields Prussian blue by exposure to the air. Most of the insoluble ferro-cyanurets are soluble without decomposition in strong sulphuric acid, and subside with their former characters on dilution with water.

The principal ferro-cyanurets are thus constituted:—

Names.	Basic Cyan.	Cyan. Iron.	Equiv.	Formulæ.
Ferro-cyan. of potassium	131.08 2 eq.	+54.39 1 eq.	=185.47	$2KCy+FeCy$.
Do. in crystals with 27 or 3 eq. of water			=212.47	
Ferro-cyan. of sodium	99.38 2 eq.	+54.39 1 eq.	=153.77	$2NaCy+FeCy$.
Do. in crystals with 108 or 12 eq. of water			=261.77	
Ferro-cyan. of barium	190.18 2 eq.	+54.39 1 eq.	=244.57	$2BaCy+FeCy$.
Do. in crystals with 54 or 6 eq. of water			=298.57	
Ferro-cyan. of strontium	140.38 2 eq.	+54.39 1 eq.	=194.77	$2SrCy+FeCy$.
Ferro-cyan. of calcium	93.78 2 eq.	+54.39 1 eq.	=148.17	$2CaCy+FeCy$.
Do. in crystals with 108 or 12 eq. of water			=256.17	
Ferro-cyan. of magnesium	78.18 2 eq.	+54.39 1 eq.	=132.57	$2MgCy+FeCy$.
Ferro-cyan. of hydrogen	54.78 2 eq.	+54.39 1 eq.	=109.17	$2HCy+FeCy$.

Ferro-cyanuret of Potassium.—This salt, called also *ferrocyanate* and *triple prussiate of potassa*, is readily prepared by digesting pure Prussian blue in solution of potassa, when a yellow liquid is obtained, which yields crystals of the same colour by evaporation. It is prepared as an article commerce by gently igniting potash with animal matters, such as blood and the horns and hoofs of animals, when cyanuret of potassium, along with some ferro-cyanuret, if iron be present, is generated. The soluble parts are taken up in water, and sulphate of protoxide of iron is added, until the Prussian blue which is formed ceases to be decomposed by the free potassa contained in the solution. The ferro-cyanuret of potassium is then set to crystallize, and is purified from sulphate of potassa by repeated crystallization.

This salt is perfectly neutral to test paper, and crystallizes readily in large transparent four-sided, nearly square, tabular crystals, derived from an acute rhombic octohedron, the apices of which are deeply truncated. It has a lemon-yellow colour, no odour, a slightly bitter taste, quite different from that of hydrocyanic acid, is insoluble in alcohol, but dissolves in less than its weight of hot water. The crystals undergo no change in the air; but when gently heated, even below 212°, or in vacuo with sulphuric acid at common temperatures, they lose all their water of crystallization, amounting to 12.82 per cent., which they recover in a moderately moist atmosphere.

This salt is much employed in preparing by double decomposition the insoluble ferro-cyanurets; and as the precipitates have in several instances very characteristic colours, ferro-cyanuret of potassium is much employed as a test. When mixed with nitrate of oxide of lead, the white ferro-cyanuret of lead is formed, lead and potassium changing places, and neutral nitrate of potassa remaining in solution; so that

$$\begin{array}{lcl} \text{1 eq. ferro-cyan. of pot. } 2KCy+FeCy & & \text{1 eq. ferro-cyan. of lead } \left\{ \begin{array}{l} 2PbCy \\ +FeCy. \end{array} \right. \\ & \text{yield} & \\ \text{2 eq. protoxide of lead } 2(Pb+O) & & \text{2 eq. potassa } \quad 2(K+O). \end{array}$$

With a salt of manganese, copper, silver, and most other metals, similar decompositions ensue. With a salt of protoxide of iron a white precipitate falls, which is perferro-cyanuret of potassium, that is, contains cyanuret of potassium united with two or more equivalents of protocyanuret of iron, and which on exposure to the air yields Prussian blue. With a persalt of iron Prussian blue is instantly generated.

Ferro-cyanuret of Sodium is prepared like the preceding salt, and crystallizes by evaporation in four-sided prisms of a yellow colour, which require 4½ times their weight of cold water for solution, and much less of boiling water. They contain 39 per cent. of water, corresponding to twelve equivalents, some of which they lose in a dry air and fall into powder.

Ferro-cyanuret of Barium is conveniently prepared by mixing hot, rather dilute, solutions made with 2 parts of ferro-cyanuret of potassium and 1 part of chloride of barium; when on cooling, and also by evaporation, ferro-cyanuret of barium separates in small rhomboidal crystals of a pale yellow colour, which require for solution 100 times their weight of boiling, and 1920 of cold, water. Of six eq. of water contained in the crystals, five and a half eq. are given off at 104°, and the remainder is retained until the heat is so high as to decompose the salt itself.

Ferro-cyanuret of Strontium is best prepared by digesting pure Prussian blue in a solution of strontia. This salt is very soluble, and crystallizes less readily than the preceding in yellow crystals. The *ferro-cyanurets of calcium and magnesium* are made in a similar manner, and are very soluble in water, the latter being very deliquescent. The former, when its solution is evaporated to the consistence of thin syrup, and kept in a warm place, crystallizes in oblique four-sided prisms of a pale yellow colour. The crystals lose eleven and a half eq. of water at 104° without loss of form, but retain the residual half equivalent until the heat is sufficient to decompose the salt itself.

When pure Prussian blue is heated with a solution of ammonia, or moist ferro-cyanuret of lead with carbonate of ammonia, a solution is obtained which by spontaneous evaporation yields small octohedral crystals of a straw-yellow colour. These crystals apparently consist of 89.08 parts or two eq. of hydrocyanate of ammonia, and 54.39 parts or one eq. of cyanuret of iron combined with one of water. When heated in a glass tube they lose their water and hydrocyanate of ammonia, leaving cyanuret of iron. On heating the solution in the open air, hydrocyanate of ammonia volatilizes, and Prussian blue is formed, oxygen gas being absorbed from the air.

Ferro-cyanuret of Hydrogen.—This compound was discovered by Mr. Porrett, and described by him under the name of *ferruretted chyazic acid* (Phil. Trans. 1814–15), the term *chyazic* being composed of the initials of carbon, hydrogen, and azote. It is now better known under the name of *ferrocyanic* or *hydroferrocyanic acid*, being regarded as a hydracid with a compound radical analogous to hydrosulphocyanic acid, a view suggested by Gay-Lussac as a deduction from the experiments of Robiquet and Berzelius. (An. de Ch. et de Ph. xv, xvii, and xxii.) In fact, on referring to its composition (page 487), it will be obvious that its formula $2HCy+FeCy$ admits of being placed in the order $2H+FeCy^3$, which represents a compound of tercyanuret of iron with two eq. of hydrogen. The supposed radical, however, has not been obtained in a separate state, nor is its composition exactly analogous to other hydracids, which contain one eq. of hydrogen combined with the radical; whereas, if regarded as ferro-cyanuret of hydrogen, it is precisely similar to other ferro-cyanurets, hydrogen being substituted for an electro-positive metal. The existence of similar double cyanurets of hydrogen goes far to establish the propriety of this view.

Two processes were recommended by Porrett for preparing this compound. The first consists in dissolving 58 grains of crystallized tartaric acid in alcohol, and mixing it with 50 grains of ferro-cyanuret of potassium dissolved in the smallest possible quantity of hot water, when bitartrate of potassa subsides, and the clear solution, by spontaneous evaporation, gradually deposites ferro-cyanuret of hydrogen in small cubic crystals of a yellow colour, which contain an undetermined quantity of water of crystallization. In the second process a solution of ferro-cyanuret of barium is decomposed by a quantity of sulphuric acid exactly sufficient for separating the barium as sulphate of baryta. Berzelius recommends that moist ferrocyanuret of lead or copper should be suspended in water and decomposed by hydrosulphuric acid, the excess of the gas be removed by a little fresh ferrocyanuret of lead, and the liquid after filtration be evaporated to dryness in vacuo along with sulphuric acid. An uncrystalline white residue is obtained, which contains one eq. of water, of which it cannot be deprived by heat without decomposition. In the process of Berzelius the hydrogen is derived from hydrosulphuric acid, the sulphur of which unites with lead; while in those of Porrett decomposed water supplies the hydrogen, and its oxygen combines with the potassium or barium.

Ferro-cyanuret of hydrogen is neither volatile nor poisonous in small quantities, is inodorous, and has an agreeably acid taste followed by slight astringency. It reddens litmus paper, neutralizes alkalies, and dissolves the alkaline carbonates with effervescence, yielding ferro-cyanurets with the metals of the alkalies. With a persalt of iron it yields Prussian blue. Its solution in open vessels is gradually decomposed by the oxygen of the air, and Prussian blue is generated, changes which are hastened by the influence of light. When its solution is boiled, hydrocyanic acid is gradually disengaged, and a white precipitate falls, which is rendered blue by the oxygen of the air. When the dry ferro-cyanuret of hydrogen is distilled, it first yields hydrocyanic acid, and then hydrocyanate and carbonate of ammonia, carburet of iron being left.

FERRO-SESQUICYANURETS.

Sesquicyanuret of iron, which has not been obtained in a solid state, acts the same part towards the basic cyanurets, as protocyanuret of iron in the ferro-cyanurets, and yields definite saline compounds, which may be termed ferro-sesquicyanurets. The principal compounds of this family are ferro-sesquicyanurets of potassium, sodium, barium, calcium, and hydrogen, all of which yield crystals of a red colour, are soluble in water, and form Prussian blue with salts of the *protoxide* of iron, for which they afford a test of great delicacy. To the same family belongs Prussian blue. These compounds are thus constituted:—

Names.	Basic Cyan.	Sesquicy.	Iron.	Equiv.	Formulæ.
Ferro-sesquicyanuret of potassium	196.62 3 eq.	+ 135.17	1 eq.	= 331.79	$3KCy+Fe^2Cy^3$.
Ditto of sodium	149.07 3 eq.	+ 135.17	1 eq.	= 284.24	$3NaCy+Fe^2Cy^3$.
Ditto of barium	285.27 3 eq.	+ 135.17	1 eq.	= 420.44	$3BaCy+Fe^2Cy^3$.
Ditto of calcium	140.67 3 eq.	+ 135.17	1 eq.	= 275.84	$3CaCy+Fe^2Cy^3$.
Ditto of hydrogen	82.17 3 eq.	+ 135.17	1 eq.	= 217.34	$3HCy+Fe^2Cy^3$.
Ditto of iron	163.17 3 eq.	+ 270.34	2 eq.	= 433.51	$3FeCy+2Fe^2Cy^3$

Ferro-sesquicyanuret of Potassium.—L. Gmelin, who discovered this family of salts, prepares this compound by transmitting through a rather dilute solution of ferro-cyanuret of potassium a current of chlorine gas, stirring the liquid continually to prevent an excess of chlorine in any one part of the solution. The process is known to be complete by the solution ceasing to give a blue precipitate with a persalt of iron which is quite free from the protoxide, or by the liquid, which at first becomes green, appearing red by transmitted light, as when held between the eye and a burning candle. The reaction of the materials is such that

2 eq. ferro-cyan. of pot. $2(2KCy+FeCy)$ and 1 eq. chlorine Cl	yield	1 eq. ferro-sesquicyan. of potassium $3KCy+Fe^2Cy^3$. and 1 eq. chlo. of potassium $K+Cl$.

The ferro-sesquicyanuret contains all the elements of two eq. of the ferrocyanuret of potassium, except one equivalent of potassium abstracted by the chlorine; but an excess of the gas is to be avoided, as it would speedily decompose the ferro-sesquicyanuret by virtue of the same affinity which caused its production. The solution after concentration deposites acicular crystals, which by solution in pure water and spontaneous evaporation crystallize in transparent anhydrous prisms of a ruby-red colour.

The ferro-sesquicyanuret of potassium is unchanged by exposure to the air, and is very sparingly soluble in alcohol. It does not precipitate salts of the peroxide of iron; but it indicates the presence of protoxide of iron dissolved in 90,000 parts of water, striking a blue or green precipitate according to the strength of the solution. When the crystals are heated, cyanogen and nitrogen gases are disengaged, and ferro-cyanuret of potassium, with a little carburet of iron, is reproduced.

The ferro-sesquicyanurets of sodium, barium, and calcium are prepared by a similar process as the foregoing salt, which they resemble in properties.

Ferro-sesquicyanuret of Hydrogen.—When the ferro-sesquicyanuret of potassium is mixed with a salt of protoxide of lead, no immediate precipitate ensues; but after a time reddish-brown crystals of ferro-sesquicyanuret of lead are deposited. On decomposing these crystals with hydrosulphuric acid gas, sulphuret of lead and ferro-sesquicyanuret of hydrogen are generated. The latter is left as a red solution, and crystallizes by spontaneous evaporation in needles of a brownish-yellow colour. This compound has an acid taste and reaction like the ferro-cyanuret of hydrogen, and ought to be viewed as a hydracid if the latter is so.

Ferro-sesquicyanuret of Iron.—This compound was accidentally discovered at Berlin in 1710, from which, and from its beautiful blue colour, it became generally known under the name of *Berlin* or *Prussian blue.* It has of late been considered as a ferrocyanate (page 489) of the peroxide of iron; but our improved knowledge of the haloid salts has caused Berzelius to place it among the double cyanurets: it may be viewed as a ferro-cyanuret of the sesquicyanuret of iron, or as a ferro-sesquicyanuret of protocyanuret of iron. To its production, therefore, the protocyanuret and sesquicyanuret of iron are both necessary. A ferro-cyanuret gives Prussian blue with a salt of the *per*oxide of iron, because by interchange of their elements sesquicyanuret of iron is generated: thus

$$\left.\begin{array}{l}\text{3 eq. ferro-cyan. of pot.}\\ \quad 3(2KCy+FeCy\\ \text{and 2 eq. peroxide of}\\ \quad \text{iron } 2(2Fe+3O)\end{array}\right\}\ \text{yield}\ \begin{array}{l}\text{1 eq. Prussian blue } 3FeCy+2Fe^2Cy^3.\\ \text{and 6 eq. potassa } \quad 6(K+O).\end{array}$$

Here the exchange lies between the peroxide of iron and cyanuret of potassium, four eq. of iron taking the place of six eq. of potassium, while six eq. of potassa unite with the acid which had been united with two eq. of peroxide of iron. *Prot*oxide of iron does not produce the same effect, because when it exchanges elements with cyanuret of potassium, protocyanuret and not sesquicyanuret of iron is generated.

When the ferro-sesquicyanuret of potassium ($3KCy+Fe^2Cy^3$) is mixed with a persalt of iron, Prussian blue is not generated, because an exchange of elements between peroxide of iron and cyanuret of potassium gives rise to sesquicyanuret and not protocyanuret of iron. But if a salt of the protoxide is present, then

$$\begin{array}{l}\left.\begin{array}{l}\text{2 eq. ferro-ses-}\\ \text{quicyan. of}\\ \text{potassium}\end{array}\right\}2(3KCy+Fe^2Cy^3)\\ \left.\begin{array}{l}\text{and 6 eq. of}\\ \text{protoxide of}\\ \text{iron}\end{array}\right\}6(Fe+O)\end{array}\ \text{yield}\ \begin{array}{l}\text{1 eq. of Prussian blue } 3FeCy+\\ \quad 2Fe^2Cy^3.\\ \text{6 eq. of potassa } \quad 6(K+O)\\ \text{and 3 eq. proto-cy. of iron } 3(Fe+Cy).\end{array}$$

Here six eq. of protocyanuret of iron and six eq. of potassa are generated; the latter unite with the acid previously combined with the protoxide of iron, three out of the six eq. of protocyanuret of iron enter into the formation of Prussian blue, and the remainder subsides along with it, or is dissolved if an excess of acid be present.

To prepare pure Prussian blue, add ferro-cyanuret of potassium to sulphate of peroxide of iron, the latter being in excess and acidulated with sulphuric acid, and both largely diluted. After the blue precipitate has subsided, draw off the clear liquor with a syphon, fill up the vessel with cold water slightly acidulated with sulphuric acid, and after subsidence again draw off the water. After repeating this process several times, first with acidulated and then with pure water, dry the precipitate in a warm place. It is then obtained in small lumps of an intensely blue colour, with a copper-red shine on its surface. The necessity for careful washing arises from the tendency of Prussian blue to combine as a double salt with ferro-cyanuret of potassium, a tendency which is observable in the ferro-cyanurets generally. Thus, Mosander finds that on mixing a concentrated solution of ferro-cyanuret of potassium with a salt of baryta, lime, or magnesia, compounds result which consist of one eq. of ferro-cyanuret of potassium with one eq. of ferro-cyanurets of barium, calcium, and magnesium. In like manner does Prussian blue combine with ferro-cyanuret of potassium, probably in two or more proportions depending on the relative quantities of the materials. If a persalt of iron is gradually mixed with a solution of ferro-cyanuret of potassium in excess, the latter falls with Prussian blue as a double salt, which is insoluble in a saline fluid, but forms a blue solution with pure water. Hence, as soon as the saline matters of the solution are washed away, the precipitate begins to dissolve, and by continually supplying pure water nearly the whole of it is removed. From some late experiments of Berzelius this soluble compound appears to consist of one eq. of Prussian blue with one eq. of ferro-cyanuret of potassium, its formula being $(2KCy+FeCy)+(3FeCy+2Fe^2Cy^3)$. When the persalt of iron is mixed in excess with ferro-cyanuret of potassium, some of the latter still falls as a double salt, which, however, is insoluble even in pure water, and contains a larger proportional quantity of Prussian blue. On washing with cold water this double salt is gradually decomposed by atmospheric oxygen: a portion of proto-cyanuret of iron is resolved into peroxide and sesquicyanuret: the latter unites with cyanuret of potassium, and is dissolved as the red ferro-sesquicyanuret, while the peroxide remains with the Prussian blue. (Berzelius in An. de Ch. et de Ph. li. 357.)

Prussian blue often contains peroxide of iron, perhaps in combination, as well as ferro-cyanuret of potassium. An instance of this has just been mentioned, and the same impurity always exists in the Prussian blue of commerce. When a protosalt of iron is precipitated with cyanuret of potassium, the orange protocyanuret quickly undergoes the same change as protochloride of iron (page 338): the iron of a portion of the protocyanuret is divided between cyanogen and oxygen from the air, forming sesquicyanuret and peroxide of iron, and the former instantly unites with the protocyanuret to constitute Prussian blue. The test for hydrocyanic acid mentioned at page 270, as well as the manufacture of Prussian blue, depends on *this change*. This pigment is prepared for the arts by fusing animal matters with pearl-ash so as to form cyanuret of potassium, which is mixed in solution with green vitriol and alum. A dirty green precipitate ensues, consisting of black oxide of iron, protocyanuret of iron, and alumina, which by exposure to the air becomes blue. Hence the Prussian blue of commerce contains as impurities hydrated alumina and peroxide of iron, combined usually with a little sulphuric acid, and ferro-cyanuret of potassium: this foreign matter may be removed by maceration in water strongly acidulated with sulphuric acid, and common Prussian blue be thus fitted for the preparation of bicyanuret of mercury and for other chemical purposes.

Pure Prussian blue is insipid and inodorous, insoluble in water and alcohol, and is not decomposed by dilute hydrochloric or sulphuric acids. Strong hydrochloric acid abstracts its iron, and causes the separation of ferro-cyanuret of hydrogen. By nitric acid it is oxidized and decomposed. Strong sulphuric acid dissolves it, forming a white compound of the aspect of gelatinous starch, from which water throws down Prussian blue in its original state. Subjected moist to the action of hydrosulphuric acid, iron filings, or powdered tin, air being excluded, it is reduced with loss of cyanogen to protocyanuret of iron; but it recovers its blue colour on exposure to the air. The alkalies exchange elements with the iron of the sesquicyanuret, separating peroxide of iron, and forming a ferro-cyanuret (page 487). Prussian blue has a strong affinity for moisture, and when dried to the utmost temperature which it can bear without decomposition, it still retains a considerable quantity of combined water. By destructive distillation it gives off water, hydrocyanate of ammonia, and carbonate of ammonia, while carburet of iron is left in the retort.

ZINCO-CYANURETS.

L. Gmelin obtained a double cyanuret of zinc and potassium in which the zinc acts as iron in the ferro-cyanurets. The zinco-cyanuret of potassium is obtained by dissolving cyanuret of zinc in a solution of cyanuret of potassium, or by dissolving hydrated oxide of zinc in a solution of cyanuret of potassium, and neutralizing with hydrocyanic acid. It is said to crystallize in large regular octohedrons, which are colourless and anhydrous. A series of zinco-cyanurets may doubtless be formed, including an acid zinco-cyanuret of hydrogen.

A cobalto-cyanuret of potassium may be prepared in the same manner as the preceding salt, and Gmelin procured it in yellow crystals similar in composition and form to ferro-cyanuret of potassium. Gmelin has also obtained similar double cyanurets with nickel and copper, and his observations have been confirmed by a late pupil of mine, Mr. F. Rodgers, and his brother (Phil. Mag. iv. 96, for 1834). From the facts collected by these chemists it is obvious that the double cyanurets offer a wide field of research, and that the ferro-cyanurets merely constitute one family of a large group of salts.

PART III.

ORGANIC CHEMISTRY.

The department of organic chemistry comprehends the history of those compounds which are of animal or vegetable origin, and which are hence called organic substances. These bodies, viewed collectively, form a remarkable contrast with those of the mineral kingdom. Such substances in general are characterized by containing some principle peculiar to each. Thus the presence of nitrogen in nitric, and of sulphur in sulphuric acid, establishes a wide distinction between these acids; and although in many instances two or more inorganic bodies consist of the same elements, as is exemplified by the compounds of sulphur and oxygen, or of nitrogen and oxygen, they are always few in number, and distinguished by a well-marked difference in the proportion in which they are united. The products of animal and vegetable life, on the contrary, consist essentially of the same elementary principles, the number of which is very limited. They are nearly all composed of carbon, hydrogen, and oxygen, in addition to which some of them contain nitrogen. Besides these, portions of phosphorus, sulphur, iron, silicic acid, potassa, lime, and other substances of a like nature, may sometimes be detected; but their quantity is exceedingly minute when compared with the principles above mentioned. In point of composition, therefore, most organic substances differ only in the proportion of their constituents, and on this account may not unfrequently be converted into one another.

The elements of organic bodies are united with each other in definite proportion, and, therefore, the same laws of combination which regulate the composition of mineral substances, must likewise influence that of organic compounds. In the latter, however, the modes of combination are generally of a complex kind. A single molecule of a metallic oxide or a chloride, as determined by its combining weight, consists of two elements, and usually of two or three atoms only. Thus, in an equivalent of potassa, the chemist has to do with a single equivalent of potassium and of oxygen, between which one kind of combination only is practicable. In an equivalent of sulphuric acid there are four atoms, which admit of three different arrangements; for S and 3O may be united as $S+3O$, or $\dot{S}+2O$, or $\ddot{S}+O$. But here, guided by the third law of combination (page 137), and by the other compounds of sulphur and oxygen, chemists infer with confidence that $S+3O$ is the true mode in which the elements of that acid are united. But in organic compounds a single combining molecule is often made up of so many elementary particles, that one is bewildered by the multiplicity of possible modes of combination. An equivalent of tartaric acid contains four eq. of carbon, two eq. of hydrogen, and five eq. of oxygen, which it is obvious may be arranged in a variety of ways; and an equivalent of quinia is composed of twenty-one eq. of carbon, twelve eq. of hydrogen, one eq. of nitrogen, and two eq. of oxygen. The difficulty of assigning any one arrangement of so many elements in preference to others equally probable, or sometimes of agreeing on any arrangement which is probable, formerly led chemists to suspect that the modes of combination in organic and inorganic bodies were essentially distinct. But the progress of analytical chemistry has in a great degree corrected this opinion, and is daily destroying the distinction between these two classes of substances. The late researches of Liebig and Wohler on the radical of benzoic acid, and those of Dumas on camphene, have indisputably established the existence of compound inflammable or electro-positive substances, which like cyanogen are susceptible of uniting with oxygen, chlorine, sulphur, and other energetic principles, and of being transferred from one to the other without a change in their own constitution. Many vegetable substances appear to consist of electro-positive compounds of carbon and hydrogen, which in some bodies exist merely as oxides, and in others act as bases in relation to water, carbonic oxide, carbonic acid, or similar compounds. In the constitution of animal matters, cyanogen appears to act an important function, as may be inferred from the history of urea and uric acid.

When organic substances are heated to redness with pure potassa or soda, they invariably yield alkaline carbonates; but at a temperature of about 400° or 450°, many of them are decomposed with formation of oxalic acid. This fact has been noticed by Gay-Lussac, who observed it with cotton, saw-dust, sugar, starch, gum, sugar of milk, and tartaric, citric, and mucic acids. The other products of course vary with the nature of the substance; but water and acetic acid are generally formed. (Quarterly Journal of Science, N. S. vi. 413.)

Organic substances, owing to the energetic affinities with which their elements are endowed, are very prone to spontaneous decomposition. The prevailing tendency of carbon and hydrogen is to appropriate to themselves so much oxygen as shall convert them into carbonic acid and water: and hence, in whatever manner these three elements may be mutually combined in a vegetable substance, they are always disposed to resolve themselves into the compounds just mentioned. If, at the time this change occurs, there is an insufficient supply of oxygen to oxidize the hydrogen and carbon completely, then, in addition to carbonic acid and water, carbonic oxide and carburetted hydrogen gases will probably be generated. One or both of these combustible products must in every case be formed, except when oxygen is freely supplied from extraneous sources; because organic bodies are so constituted that their oxygen is never in sufficient quantity for converting the carbon into carbonic acid, and the hydrogen into water.

If substances composed of oxygen, hydrogen, and carbon, are liable to spontaneous decomposition, that tendency should become much stronger when nitrogen is also present. Other and powerful affinities are then superadded to those above enumerated, and especially that of hydrogen for nitrogen. Such compounds are very prone to decomposition, and the usual products are water, carbonic acid, hydrocyanic acid, and ammonia.

Another circumstance which is characteristic of organic products is the impracticability of forming them artificially by direct union of their elements, the tendency of those elements being to unite so as to form water and carbonic acid. Some organic bodies are developed during the decomposition of others, as, for instance, oxalic acid from most substances when digested in nitric acid, alcohol from sugar, and acetic acid in the distillation of wood; but these results do not strictly form exceptions to the preceding remark.

Animal and vegetable substances are decomposed by a red heat, and nearly all are partially affected by a temperature far below ignition. When heated in the open air, or with substances which yield oxygen freely, they burn, and are converted into water and carbonic acid; but if exposed to heat in vessels from which atmospheric air is excluded, very complicated products ensue. A compound, consisting of carbon, hydrogen, and oxygen, yields water, carbonic acid, carbonic oxide, carburetted hydrogen of various kinds, and probably pure hydrogen. Besides these products, some acetic acid is commonly generated, together with a volatile oil which has a dark colour and burnt odour, and is hence called empyreumatic oil. An azotized substance, in addition to these, yields ammonia, cyanogen, and probably free nitrogen.

From the foregoing remarks, it appears that organic products are characterized by the following circumstances:—1st, by being composed of the same elements; 2nd, by the facility with which they undergo spontaneous decomposition; 3rd, by the impracticability of forming them by the direct union of their elements; and 4th, by being decomposed at a red heat.

VEGETABLE CHEMISTRY.

All bodies which are of vegetable origin are termed vegetable substances. They are nearly all composed of oxygen, hydrogen, and carbon, and in a few of them nitrogen is likewise present. Every distinct compound which exists ready formed in plants, is called a *proximate* or *immediate principle* of vegetables. Thus sugar, starch, and gum are proximate principles. Opium, though obtained from a plant, is not a proximate principle; but consists of several proximate principles mixed more or less intimately with each other.

The proximate principles of vegetables are sometimes distributed over the whole plant, while at others they are confined to a particular part. The methods by which they are procured are very variable. Thus gum exudes spontaneously, and the saccharine juice of the maple-tree is obtained by incisions made in the bark. In some cases a particular principle is mixed with such a variety of others, that a distinct process is required for its separation. Of such processes consists the *proximate analysis* of vegetables. Sometimes a substance is separated by mechanical means, as in the preparation of starch. On other occasions, advantage is taken of the volatility of a compound, or of its solubility in some particular menstruum. Whatever method is employed, it should be of such a nature as to occasion no change in the composition of the body to be prepared.

The reduction of the proximate principles into their simplest parts constitutes their *ultimate analysis*. By this means chemists ascertain the quantity of oxygen, carbon, and hydrogen present in any compound. The former method of performing this operation was by what is termed *destructive distillation;* that is, by exposing the compounds to a red heat in close vessels, and collecting all the products. So many different substances, however, are procured in this way, such as water, carbonic acid, carbonic oxide, carburetted hydrogen, and the like, that it is almost impossible to arrive at a satisfactory conclusion. A more simple and effectual method was proposed by Gay-Lussac and Thenard in the second volume of their celebrated *Recherches Physico-Chimiques*. The object of their process, which is applicable to the ultimate analysis of animal as well as vegetable substances, is to convert the whole of the carbon into carbonic acid, and the hydrogen into water, by means of some compound which contains oxygen in so loose a state of combination as to give it up to those elements at a red heat.

The agent first employed by these chemists was chlorate of potassa. This substance, however, is liable to the objection, that it not only gives oxygen to the substance to be analyzed, but is itself decomposed by heat. On this account it is now very rarely employed in ultimate analysis, oxide of copper, proposed by Gay-Lussac, having been substituted for it. This oxide, if alone, may be heated to whiteness without parting with oxygen; whereas it yields oxygen readily to any combustible substance with which it is ignited. It is easy, therefore, by weighing it before and after the analysis, to discover the precise quantity of oxygen which has entered into union with the carbon and hydrogen of the substances submitted to examination.

The ultimate analysis of organic bodies is one of the most delicate operations with which the analytical chemist can be engaged. The chief cause of uncertainty in the process arises from the presence of moisture, which is retained by some animal and vegetable substances with such force, that it can be expelled only by a temperature which endangers the decomposition of the compound itself. The best mode of drying organic matters for the purpose, is by confining them with sulphuric acid under the exhausted receiver of an air-pump, and exposing them at the same time to a temperature of 212°,—a method adopted by Berzelius, and for which a neat apparatus has been described by Dr. Prout. (An. of Phil. vi. 272.) Another source of difficulty is occasioned by atmospheric air within the apparatus, owing to the presence of which nitrogen may be detected in the products, without having been contained in the substance analyzed.

But though the ultimate analysis of organic substances is difficult in practice, in theory it is exceedingly simple. It consists in mixing three or four grains of the body to be analyzed with about two hundred grains of oxide of copper, heating the mixture to redness in a glass tube, and collecting the gaseous products in a graduated glass jar over mercury. From the quantity of carbonic acid procured by measure, its weight may readily be inferred (page 187); and from this, the quantity of carbonaceous matter may be calculated, by recollecting that every 22.12 grains of the acid contain 16 of oxygen and 6.12 of carbon.

In order to ascertain the quantity of hydrogen, the gaseous products are transmitted through a tube filled with fragments of fused chloride of calcium, which absorbs all the watery vapour; and by its increase in weight indicates the precise quantity of that fluid generated. Every 9 grains of water thus collected correspond to 1 grain of hydrogen and 8 of oxygen.

If the quantity of oxygen contained in the carbonic acid and water corresponds precisely to that lost by the oxide of copper, it follows that the organic substance itself was free from oxygen. But if, on the other hand, more oxygen exists in the products than was lost by the copper, it is obvious that the difference indicates the amount of oxygen contained in the subject of analysis.

If nitrogen enter into the constitution of the organic substance, it will pass over in the gaseous state, mixed with carbonic acid; and its quantity may be ascertained by removing the carbonic acid by means of a solution of pure potassa. In order to prevent the production of binoxide of nitrogen, which is otherwise apt to be generated, the oxide should be mixed with some metallic copper; or the latter may be placed on the surface of the oxide, and be kept at a red heat, in order that any oxide of nitrogen, in passing through the metallic mass, should be decomposed. The copper for the purpose should be in a state of fine division, and is best prepared from the oxide by means of hydrogen gas.

It need scarcely be observed, that if the analysis has been successfully performed, the weight of the different *products*, added together, should make up the exact weight of the organic substance employed.

In analyzing an animal or vegetable fluid, the foregoing process will require slight modification. If the fluid is of a fixed nature, it may be made into a paste with oxide of copper, and heated in the usual manner. But if it is volatile, a given weight of its vapour is conducted over oxide of copper heated to redness in a glass tube.

The constitution of vegetable substances is not yet sufficiently known to admit of their being classified in a purely scientific order. I have arranged them into seven sections: the first includes the vegetable acids; the second, the vegetable alkalies; the third comprises neutral substances, the oxygen and hydrogen of which are in the same ratio as in water; the fourth contains oleaginous, resinous, and bituminous principles; the fifth, spirituous and ethereal principles; the sixth, colouring matters; and the seventh comprehends substances not referable to preceding sections.

SECTION I.

VEGETABLE ACIDS.

Those compounds are regarded as vegetable acids which possess the properties of an acid, and are peculiarly the product of vegetation. These acids, like all organic principles, are decomposed by a red heat. They are in general less liable to spontaneous decomposition than other vegetable substances. They are nearly all decomposed by concentrated hot nitric acid, by which they are converted into carbonic acid and water. They do not possess any constant analogy in composition. It was thought at one time that their oxygen was always more than sufficient to convert all their hydrogen into water; but several acids are known in which, as in sugar, the oxygen and hydrogen are in the same ratio as in water, and in benzoic acid the hydrogen is actually in excess. It seems, however, to be true that all vegetable substances are acid, which contain more oxygen than suffices to form water with their hydrogen. The following table exhibits the constituents of the principal vegetable acids, and will serve to show analogies of composition. The formulæ merely express the elements contained in an equivalent of each acid, without indicating the order in which they are arranged. The composition, where not otherwise expressed, indicates the anhydrous acids, such as they exist in combination with an alkali: the numeral attached to each symbol expresses the number of equivalents of that element contained in the acid.

Names of acids.	Carb.	Hyd.	Oxyg.	Equiv.	Formulæ.
Oxalic	12.24+	0+	24=	36.24	C^2O^3.
Do. sublimed with 9 parts or 1 eq. of water			=	45.24	
Do. in crystals from solution with 27 parts or 3 eq. of water			=	63.24	
Mellitic	24.48+	0+	24=	48.48	C^4O^3.
Croconic	30.6 +	0+	32=	62.6	C^5O^4.
Acetic	24.48+	3+	24=	51.48	$C^4H^3O^3$.
Do. in crystals with 9 parts or 1 eq. of water			=	60.48	
Lactic (in lactate of oxide of zinc)	36.72+	5+	40=	81.72	$C^6H^5O^5$.
Do. dried in vacuo from solution with 9 parts or 1 eq. of water			=	90.72	
Do. sublimed	36.72+	4+	32=	72.72	$C^6H^4O^4$.
Kinic	91.8 +	10+	80=	181.8	$C^{15}H^{10}O^{10}$.
Malic	24.48+	2+	32=	58.48	$C^4H^2O^4$.
Citric	24.48+	2+	32=	58.48	$C^4H^2O^4$.
Pyrocitric	61.2 +	2+	24=	87.2	$C^{10}H^2O^3$.
Tartaric	24.48+	2+	40=	66.48	$C^4H^2O^5$.
Do. in crystals with 9 parts or 1 eq. of water			=	75.48	
Racemic	24.48+	2+	40=	66.48	$C^4H^2O^5$.
Do. in crystals with 18 parts or 2 eq. of water			=	84.48	
Benzoic	85.68+	5+	24=	114.68	$C^{14}H^5O^3$.
Do. in crystals with 9 parts or 1 eq. of water			=	123.68	
Meconic	42.84+	2+	56=	100.84	$C^7H^2O^7$.
Metameconic	73.44+	4+	80=	157.44	$C^{12}H^4O^{10}$.
Tannic (from catechu)	110.16+	9+	64=	183.16	$C^{18}H^9O^8$.
——— (from gall-nuts)	110.16+	9+	96=	215.16	$C^{18}H^9O^{12}$.
Gallic	42.84+	3+	40=	85.84	$C^7H^3O^5$.
Do. in crystals with 9 parts or 1 eq. of water			=	94.84	
Pyrogallic	36.72+	3+	24=	63.72	$C^6H^3O^3$.
Metagallic	73.44+	3+	24=	100.44	$C^{12}H^3O^3$.
Ellagic	42.84+	2+	32=	76.84	$C^7H^2O^4$.
Succinic	24.48+	2+	24=	50.48	$C^4H^2O^3$.

Names of acids.	Carb. Hyd. Oxyg. Equiv.	Formulæ.
Mucic	36.72 + 5 + 64 = 105.72	$C^6H^5O^8$.
Camphoric	122.4 + 16 + 40 = 178.4	$C^{20}H^{16}O^5$.
Valerianic	61.2 + 9 + 24 = 94.2	$C_{10}H^9O^3$.
Rosellic	97.92 + 16 + 32 = 145.92	$C_{16}H^{16}O^4$.

Oxalic Acid.

Oxalic acid exists ready formed in several plants, especially in the *rumex acetosa* or common sorrel, and in the *oxalis acetosella* or wood sorrel; but it almost always occurs in combination either with lime or potassa. These plants contain binoxalate of potassa; and the oxalate of lime has been found in large quantity by M. Braconnot in several species of lichen.

Oxalic acid is easily made artificially by digesting sugar in five or six times its weight of nitric acid, and expelling the excess of that acid by distillation, until a fluid of the consistence of syrup remain in the retort. The residue in cooling yields crystals of oxalic acid, the weight of which amounts to rather more than half the quantity of the sugar employed. They should be purified by repeated solution in pure water, and re-crystallization; for they are very apt to retain traces of nitric acid, the odour of which becomes obvious when the crystals are heated. In the conversion of sugar into oxalic acid, changes of a very complicated nature ensue, during which a large quantity of binoxide of nitrogen with some carbonic acid is disengaged: water is freely generated at the same time, and a small quantity of malic and acetic acids is produced. As oxalic acid does not contain any hydrogen, and has a smaller proportional quantity of carbon than sugar, there can be no doubt that the production of this acid essentially depends upon the sugar being deprived of all its hydrogen and a portion of its carbon by oxygen derived from the nitric acid.

Many organic substances besides sugar, such as starch, gum, most of the vegetable acids, wool, hair, and silk, are converted into oxalic by the action of nitric acid;—a circumstance which is explicable on the fact that oxalic acid contains more oxygen than any other principle, whether of animal or vegetable origin. It is also generated by heating organic substances with potassa. (Page 494.)

Oxalic acid crystallizes in slender, flattened, four and six-sided prisms terminated by two-sided summits; but their primary form is an oblique rhombic prism. It has an exceedingly sour taste, reddens litmus paper strongly, and forms neutral salts with alkalies. The crystals, which consist of one equivalent of real acid and three of water, undergo no change in ordinary states of the air; but when the atmosphere is very dry, or the temperature slightly raised, as to 70° or 80°, partial efflorescence ensues, and at 212° they lose two equivalents of water, which on exposure to the air while cold they soon recover. Heated in a tube to 209° they fuse in their water of crystallization, and are hence soluble in boiling water without limit: at 50° they dissolve in 15.5 times their weight of water, and in 9.5 times at 57°; but the solubility is increased by the presence of nitric acid. They are dissolved also by alcohol, though less freely than in water.

Oxalic acid possesses considerable volatility. Mr. Faraday has shown that a very slow sublimation of oxalic acid takes place at common temperatures. At 212° its vaporization goes on in appreciable quantities; and at 330° the acid, when deprived of two equivalents of its water of crystallization, sublimes rapidly, and without any decomposition. The sublimed acid crystallizes in transparent acicular crystals, which contain one equivalent of water; but by exposure to the air they rapidly absorb moisture, and become opaque. (An. of Phil. N. S. x. 348.) When fully hydrated oxalic acid is suddenly heated to about 300°, it undergoes decomposition, and yields water, carbonic acid gas mixed with carbonic oxide in the ratio of 6 to 5, and formic acid. To this change, which has been lately studied by Gay-Lussac, the water of crystallization essentially contributes, the elements of formic acid being such, that it may be considered a compound of two equivalents of carbonic oxide with one equivalent of water. The crystals, when deprived of 2-3ds of their water, are much more stable, not suffering the same decomposition until the heat exceeds 330°, and even then a considerable portion is sublimed.

Oxalic acid is a powerful and rapidly fatal poison; and frequent accidents have occurred from its being sold and taken by mistake for Epsom salt, with the appearance of which its crystals have some resemblance. These substances may be easily distinguished, however, by the strong acidity of oxalic acid, which may be tasted without danger, while sulphate of magnesia is quite neutral, and has a bitter saline taste. In cases of poisoning with this acid, chalk mixed with water should be administered as an antidote, an insoluble oxalate being formed, which is inert. Chalk was first suggested for this purpose by my colleague, Dr. A. T. Thomson; and his opinion has been since fully confirmed by the experiments of Drs. Christison and Coindet, who have recommended the use of magnesia with the same intention. (Christison on Poisons.)

Oxalic acid is easily distinguished from all other acids by the form of its crystals, and by its solution giving with lime-water a white precipitate, which is insoluble in an excess of the acid. When the acid is contained in mixed fluids, it may be conveniently precipitated by nitrate of oxide of lead, care being taken beforehand to neutralize the solution with a little carbonate of soda. The precipitated oxalate of oxide of lead, after being well washed, and while yet moist, is suspended in water, and decomposed by a current of hydrosulphuric acid: the clear liquid is poured off or filtered from the sulphuret of lead, and concentrated by evaporation that crystals may form. These may be purified by solution in pure water and a second crystallization.

As an equivalent of oxalic acid contains two. eq. of carbon and three of oxygen, it may be regarded either as a direct compound of carbon and oxygen, indicated by the formula $\underline{\dddot{C}}$ or $C{\cdot}O^3$, or as a compound of carbonic oxide and carbonic acid, denoted by $\dot{C}+\ddot{C}$. The latter is supported by the fact observed by Döbereiner, that oxalic acid is converted into carbonic oxide and carbonic acid gases by the action of concentrated sulphuric acid. The decomposition takes place slowly at 212°, and rapidly at 230°.

The neutral oxalates of protoxides consist of 36.24 parts or one eq. of oxalic and one eq. of the base, the general formula of such salts being $\dot{M}+\underline{\dddot{C}}$, or $\dot{M}+\overline{O}$ (page 152). Most of these compounds are either insoluble or sparingly soluble in water; but they are all dissolved by the nitric, and also by the hydrochloric acid, except when the latter precipitates the base of the salts. The only oxalates which are remarkable for solubility are those of potassa, soda, lithia, ammonia, alumina, and peroxide of iron.

A soluble oxalate is easily detected by adding to its solution a neutral salt of lime or oxide of lead, when a white oxalate of those bases will be thrown down. On digesting the precipitate in a little sulphuric acid, an insoluble sulphate is formed, and the solution yields crystals of oxalic acid on cooling. All insoluble oxalates, the bases of which form insoluble compounds with sulphuric acid, may be decomposed in a similar manner. All other insoluble oxalates may be decomposed by potassa, by which means a soluble oxalate is procured.

The oxalates, like all salts which contain a vegetable acid, are decomposed by a red heat, a carbonate being left, provided the oxide can retain carbonic acid at the temperature which is employed. As oxalic acid is so highly oxidized, its salts leave no charcoal when heated in close vessels.

Several oxalates are reduced to the metallic state, with evolution of pure carbonic acid, when heated to redness in close vessels. (Pages 348 and 351.) The peculiar constitution of oxalic acid accounts for this change; for one equivalent of the acid, to be converted into carbonic acid, requires precisely one equivalent of oxygen, which is the exact quantity contained in the oxide of a neutral protoxalate.

Oxalates of Potassa.—Oxalic acid forms with potassa three compounds, which were first described by Wollaston. (Philos. Trans. 1808.) The first is the neutral oxalate, which is formed by neutralizing carbonate of potassa with oxalic acid. It crystallizes in oblique quadrangular prisms, which have a cooling bitter taste, require about twice their weight of water at 60° for solution, and contain 36.24 parts or one eq. of oxalic acid, 47.15 or one eq. of potassa, and 9 parts or one eq. of water. This salt is much employed as a reagent for detecting lime. The binoxalate is contained in sorrel, and may be procured from that plant by solution and crystallization. It crystallizes readily in small rhomboids, which are less soluble in water than the neutral oxalate, and consist of 72.48 parts or two eq. of acid, 47.15 or one eq. of potassa, and 18 or two eq. of water. It is often sold under the name of *essential salt of lemons* for removing iron moulds from linen;—an effect which it produces by half of its acid uniting with the peroxide of iron and forming a soluble oxalate. The quadroxalate is the least soluble of these salts, and is formed by digesting the binoxalate in nitric acid, by which it is deprived of half of its base. The crystals consist of 144.96 parts or four eq. of acid, 47.15 or one eq. of potassa, and 63 or seven eq. of water.

Oxalate of Soda may be made in the same manner as oxalate of potassa. It likewise forms a binoxalate, but no quadroxalate is known.

Oxalate of Ammonia.—This salt, prepared by neutralizing ammonia with oxalic acid, is much used as a reagent. It is very soluble in hot water, and is deposited in acicular crystals when a saturated hot solution is allowed to cool. The crystals contain two equivalents of water. Dr. Thomson has likewise described a binoxalate of ammonia, which is less soluble than the preceding, and contains three equivalents of water.

During the decomposition of oxalate of ammonia by heat an interesting compound is generated, which was discovered and described by Dumas, who has given it the name of *oxalammide* or *oxamide*, compounded of the words *oxalic* and *ammonia*. (An. de Ch. et de Ph. xliv. 129.) On putting oxalate of ammonia into a retort and applying heat, the crystals at first lose water and become opaque; then the salt, where directly in contact with the hot glass, fuses, boils, and disappears; and this action goes on successively through the mass, until, excepting traces of a light carbonaceous matter, the whole is expelled. During the whole course of the distillation gas is disengaged: at first ammonia appears, then a mixture of carbonic acid and carbonic oxide, the former of which unites with the ammonia, and towards the close of the process cyanogen gas is generated. The oxamide, which constitutes but a small part of the products, is found as a thick deposite, of a dirty white colour, in the neck of the retort, and partly floating in flakes in the water of the recipient. It is separated from adhering carbonate of ammonia by being well washed with cold water.

Oxamide is insoluble in cold water: at 212° it is dissolved, and is deposited unchanged on cooling in the form of flocks of a dirty white colour, and of a confused crystalline appearance. Heated gently in an open tube it speedily rises in vapour, and is condensed again on the cold part of the tube; but when sharply heated in a retort, it enters into fusion, and while part sublimes, another portion yields cyanogen gas, and leaves a very bulky carbonaceous residue.

The elements contained in oxamide are expressed by the formula $2C+N+2H+2O$. Nothing certain is known respecting the mode in which these elements are arranged; but the three following hypotheses are most consistent with known affinities:—it may be a compound of

Cyanogen and water	$(2C+N)+2(H+O)$
Or binoxide of nitrogen and olefiant gas	$(2H+2C)+(N+2O)$
Or dinituret of hydrogen and carbonic oxide	$(2H+N)+2(C+O)$.

It can scarcely be thought to contain either oxalic acid or ammonia. But when boiled with a solution of potassa, ammonia after a short time is evolved, and oxalate of potassa generated; and when heated with a large excess of strong sulphuric acid, a mixture of carbonic oxide and carbonic acid gases, in the ratio to form oxalic acid, is evolved, and sulphate of ammonia is produced. Under the influence of the attraction of potassa for oxalic acid, or of sulphuric acid for ammonia, oxamide and water interchange elements; so that

1 eq. oxamide	$2C+N+2H+2O$	yield	1 eq. oxalic acid	$2C+3O$
and 1 eq. water	$H+O$		and 1 eq. ammonia	$3H+N$.

Oxalate of Lime.—This salt, like all the insoluble oxalates, is easily prepared by way of double decomposition. It is a white finely divided powder, which is remarkable for its extreme insolubility in pure water. On this account a soluble oxalate is an exceedingly delicate test for lime. It is soluble, however, in hydrochloric and nitric acids. It is composed of 36.24 parts or one eq. of oxalic acid, and 28.5 or one eq. of lime. It may be exposed to a temperature of 560° without decomposition, and is then quite anhydrous. No binoxalate of lime is known.

This salt is interesting in a pathological point of view, because it is a frequent ingredient of urinary concretions, being the basis of what is called the *mulberry calculus.*

Oxalate of Magnesia may be prepared by mixing oxalate of ammonia with a hot concentrated solution of sulphate of magnesia. It is a white powder, which is very sparingly soluble in water; but, nevertheless, when sulphate of magnesia is moderately diluted with cold water, oxalate of ammonia occasions no precipitate. On this fact is founded the best analytic process for separating lime from magnesia.

Oxalate of Chromium and Potassa.—This salt was discovered by my brother during the winter of 1830–31, by adding oxalic acid to a solution of bichromate of potassa until effervescence ceased, and then evaporating. The same salt has been prepared independently, and by a better process, by Dr. Gregory, who employs 190 parts of bichromate of potassa, 157.5 of oxalic acid in crystals, and 517.5 of crystals of binoxalate of potassa, pours hot water over the materials, and when effervescence has ceased concentrates very considerably. This beautiful salt crystallizes in thin elongated prisms, which appear black by reflection, blue by transmitted light, and green when reduced to powder: its solution is green and red at the same time, except by candlelight, when it is of a pure red. Dr. Gregory considers it a compound of three eq. of oxalic acid, two of potassa, one of green oxide of chromium, and six of water.

Mellitic Acid.—This acid is contained in the rare substance called *honeystone*, which is occasionally met with at Thuringia in Germany. The honeystone, according to Klaproth, is a mellitate of alumina, and on boiling it in a large quantity of water, the acid is dissolved, and the alumina subsides. On concentrating the solution, mellitic acid is deposited in minute acicular crystals. From its rarity it has been little studied. Liebig and Wöhler have shown (page 497) that it has the same composition as succinic acid, hydrogen excepted. (An. de Ch. et de Ph. xliii. 200.)

Croconic Acid.—In the preparation of potassium from cream of tartar (page 294), the principal products are potassium and carbonic oxide gas; but these are accompanied with dense fumes, which in cool vessels deposite a gray flaky substance. On the addition of water this matter becomes red, and on exposure to the air a reddish-yellow solution is formed, which by gentle evaporation yields croconate of potassa in crystals of the same colour as the solution; the residual liquid contains bicarbonate and oxalate of potassa. In order to separate croconic acid, the crystals, purified by a second crystallization and reduced to fine powder, are put into absolute alcohol, to which sulphuric acid of specific gravity 1.78, in quantity insufficient for combining with all the alkali of the croconate, is added. The mixture is gently warmed during several hours, and frequently shaken, until a drop of the solution, mixed with chloride of barium, causes no turbidity. The yellow alcoholic solution of croconic acid is then separated from the sulphate of potassa by filtration, and the acid obtained by expelling the alcohol. (Gmelin's Handbuch.)

Croconic acid, by solution in water and spontaneous evaporation, yields transparent prismatic crystals of a yellow colour, which are inodorous, have an acid astringent taste, redden litmus, and neutralize alkaline bases. It bears a heat of 212° without decomposition, but at a higher temperature it is decomposed, giving a deposite of charcoal. A similar facility of decomposition is conspicuous in all its salts: when, for instance, croconate of potassa is heated, it takes fire at a temperature below ignition, the whole mass blackens, and is found to be a mixture of charcoal and carbonate of potassa. As it consists of carbon and oxygen in the ratio of five eq. of carbon to four eq. of oxygen, its origin seems referable to the deoxidizing action of potassium on carbonic acid and carbonic oxide.

Acetic Acid.

Acetic acid exists ready formed in the sap of many plants, either free or combined with lime or potassa: it is generated during the destructive distillation of vegetable matter, and is an abundant product of the acetous fermentation.

Common vinegar, the acidifying principle of which is acetic acid, is commonly prepared in this country by fermentation from an infusion of malt, and in France from the same process taking place in weak wine. Vinegar, thus obtained, is a very impure acetic acid, containing the saccharine, mucilaginous, glutinous, and other matters existing in the fluid from which it was prepared. It is separated from these impurities by distillation. Distilled vinegar, formerly called *acetous acid*, is real acetic acid merely diluted with water, and commonly containing a small portion of empyreumatic oil, formed during the distillation, and from which it receives a peculiar flavour. It may be rendered stronger by exposure to cold, when a considerable part of the water is frozen, while the acid remains liquid.

The acid now generally employed for chemical purposes is prepared by the distillation of wood, and is sold under the name of *pyroligneous acid*. When first made it is very impure, and of a dark colour, holding in solution tar and volatile oil. In this state it is mixed with chalk, and obtained in the state of acetate of lime, which is decomposed by digestion with sulphate of soda: the resulting acetate of soda is then fused at a high temperature, insufficient to decompose the salt, but sufficient to expel or char the impurities. The acetate of soda is thus obtained pure and in crystals, and is decomposed by sulphuric acid.

Concentrated acetic acid is best obtained by decomposing the acetates either by sulphuric acid, or in some instances by heat. A convenient process is to distil acetate of potassa with half its weight of concentrated sulphuric acid, the recipient being kept cool by the application of ice. The acid is at first contaminated with sulphurous acid; but by mixing it with a little peroxide of manganese, and redistilling, it is rendered quite pure. A strong acid may likewise be procured from acetate of oxide of copper by the sole action of heat. The acid when first collected has a greenish tint, owing to the presence of copper, from which it is freed by a second distillation. Pyro-acetic ether is formed towards the close of the process.

Strong acetic acid is exceedingly pungent, and even raises a blister when kept for some time in contact with the skin. It has a very sour taste and an agreeable refreshing odour. Its acidity is well marked, as it reddens litmus paper powerfully, and forms neutral salts with the alkalies. It is exceedingly volatile, rising rapidly in vapour at a moderate temperature without undergoing any change. Its vapour is inflammable, and burns with a white light. In its most concentrated form it is a definite compound of one equivalent of water, and one equivalent of acid; and in this state it crystallises when exposed to a low temperature, retaining its solidity until the thermometer rises to 50° F. It is decomposed by being passed through red-hot tubes; but owing to its volatility, a large quantity of it escapes decomposition.

The only correct mode of estimating the strength of acetic acid is by its neutralizing power. Its specific gravity is no criterion, as will appear from the following table (Thomson's First Principles, vol. ii. p. 135), exhibiting the density of acetic acid of different strengths.

Acid.	Water.	Sp. gr. at 60° F.
1 atom	+ 1 atom	1.06296
1	+ 2	1.07060
1	+ 3	1.07080
1	+ 4	1.07132
1	+ 5	1.06820
1	+ 6	1.06708
1	+ 7	1.06349
1	+ 8	1.05974
1	+ 9	1.05794
1	+10	1.05439

The acetic is distinguished from all other acids by its flavour, odour, and volatility. Its salts, which are called *acetates*, are all soluble in hot and most of them in cold water, are destroyed by a high temperature, and are decomposed by sulphuric acid. The neutral acetates of protoxides consist of 51.48 parts or one eq. of anhydrous acetic acid and one eq. of base, so that the general formula of such salts is $\dot{M}+C^4H^3O^3$, or $\dot{M}+\bar{A}$, $\bar{A}$ being used as the symbol of one equivalent of acetic acid, and M of any electro-positive metal.

Acetate of Potassa.—This salt is made by neutralizing the carbonate with acetic acid, or by decomposing acetate of lime with sulphate of potassa. When cautiously evaporated, it forms irregular crystals, which are obtained with difficulty, owing to the deliquescent property of the salt. According to Dr. Thomson, the crystals are composed of 98.63 parts or one eq. of neutral acetate of potassa, and 18 or two eq. of water. It is commonly prepared for pharmaceutic purposes by evaporating the solution to dryness, and heating the residue so as to cause the igneous fusion. On cooling it becomes a white crystalline foliated mass, which is generally alkaline.

This salt is highly soluble in water, and requires twice its weight of boiling alcohol for solution.

Dr. Thomson procured a binacetate by mixing acetic acid and carbonate of potassa in the proportion of two equivalents of the former to one of the latter. On confining the solution along with sulphuric acid under the exhausted receiver of an air-pump, the binacetate was deposited in large transparent flat plates. The crystals contain six equivalents of water, and deliquesce rapidly on exposure to the air.

Acetate of Soda is prepared in large quantity by manufacturers of pyroligneous acid by neutralizing the impure acid with chalk, and then decomposing the acetate of lime by sulphate of soda. It crystallizes readily by gentle evaporation, and its crystals, which are not deliquescent, are composed of 51.48 parts or one eq. of acetic acid, 31.3 parts or one eq. of soda, and 54 parts or six equivalents of water. (Berzelius and Thomson.) The form of its crystals is very complicated, and derived from an oblique rhombic prism. (Brooke.) When heated to 550°, it is deprived of its water, and undergoes the igneous fusion without parting with any of its acid. At 600° decomposition takes place.

Acetate of soda is much employed for the preparation of concentrated acetic acid.

Acetate of Ammonia is made by neutralizing the carbonate with acetic acid. It crystallizes with difficulty in consequence of being deliquescent and highly soluble. It has been long used in medicine as a febrifuge under the name of *spirit of Mindererus.*

The *Acetates of Baryta, Strontia, and Lime* are of little importance. The former, which is occasionally employed as a reagent, crystallizes in irregular six-sided prisms terminated by dihedral summits, the primary form of which is a right rhomboidal prism. The latter crystallizes in very slender acicular crystals of a silky lustre, and is chiefly employed in the preparation of acetate of soda.

Acetate of Alumina is formed by adding acetate of oxide of lead to sulphate of alumina, when the sulphate of oxide of lead subsides, and acetate of alumina remains in solution. It is used by dyers and calico printers as a basis or mordant.

Acetates of Protoxide of Lead.—The *neutral acetate*, long known by the names of sugar of lead (*saccharum Saturni*) and *cerussa acetata*, is made by dissolving either the carbonate or litharge in distilled vinegar. The solution has a sweet, succeeded by an astringent taste, does not redden litmus paper, and deposites shining acicular crystals by evaporation. When more regularly crystallized, it occurs in six-sided prismatic crystals, cleaveable parallel to the lateral and terminal planes of a right rhombic prism, which may be regarded as its primary form. (Mr. Brooke.) The crystals effloresce slowly by exposure to the air, and require about four times their weight of water at 60° for solution. They consist of 51.48 parts or one eq. of the acid, 111.6 parts or one eq. of protoxide of lead, and 27 parts or three equivalents of water.

This salt is partially decomposed, with formation of carbonate of *oxide* of lead, by water which contains carbonic acid, or by exposure to the air; but a slight addition of acetic acid renders the solution quite clear. It is much used in the arts, in medical and surgical practice as a sedative and astringent, and in chemistry as a reagent.

The *subacetate*, commonly called *extractum Saturni*, is prepared by boiling 1 part of the neutral acetate, and 2 parts of litharge, deprived of carbonic acid by heat, with 25 parts of water.

This salt is less sweet and more soluble in water than the neutral acetate, and has an alkaline reaction. Thenard has obtained it by evaporation in opaque white tabular crystals, but it crystallizes with difficulty. It is decomposed by a current of carbonic acid, with production of pure carbonate of oxide of lead; and forms a turbid solution, owing to the formation of the carbonate, when it is mixed with water in which carbonic acid is present. It consists of one equivalent of acid, and three equivalents of protoxide of lead, and is, therefore, a *triacetate.* (Berzelius.)

A *diacetate* may be formed by boiling with water a mixture of litharge and acetate of oxide of lead in atomic proportion. (Thomson.)

Acetates of Protoxide of Copper.—These salts have been carefully studied by Berzelius and Phillips. (An. of Phil. N. S. i. ii. iv. and viii.) The *neutral acetate* may be formed either by dissolving protoxide of copper or common verdigris in acetic acid, or by decomposing the sulphate by an equivalent quantity of acetate of oxide of lead. On evaporation it readily crystallizes in rhombic octohedrons of a dark green colour, which are soluble in 20 times their weight of cold water, in 5 of boiling water, and in 14 of boiling alcohol. The crystals consist of 39.6 parts or one eq. of the black oxide, 51.48 parts or 1 eq. of acetic acid, and 9 parts or one equivalent of water.

When copper plates are covered with a layer of the neutral acetate, made into a thin paste with water, and are then exposed for about two months to a moist atmosphere, a sub-salt is generated, which appears in crystalline blue scales and needles of a silky lustre. It is a *diacetate*, consisting of two equivalents of the black oxide and one of acetic acid, united with six equivalents of water. At 212° it loses part of its water and acquires a pretty green tint. When freely mixed with water it is converted into the soluble neutral acetate, and into an insoluble triacetate. The diacetate is the principal ingredient of the blue-coloured varieties of verdigris.

The *triacetate*, besides being formed by the action of water on the diacetate, is obtained as a light green powder by digesting the hydrated oxide with the neutral acetate. It is also generated when ammonia is cautiously added to a solution of the neutral acetate: in a cold solution the precipitate is uncrystalline and of a green colour, which by washing passes into blue; while in a hot solution the precipitate is granular, and of a dirty grayish-green tint. By the continued action of water, freely employed, it may be resolved into oxide and neutral acetate of copper. It consists of three equivalents of oxide, one of acid, and one and a half of water.

Another sub-salt, composed of three equivalents of oxide, two of acid, and six of water, is generated by adding to a strong boiling solution of the neutral acetate, a small quantity of ammonia insufficient to produce a permanent precipitate of the triacetate. The sub-salt in question, which is sparingly soluble in cold water, separates on cooling, and should be washed with alcohol. It is considered by Berzelius as the principal ingredient of the green varieties of verdigris.

The pigment, *verdigris*, which is a variable mixture of the subacetates, is prepared in large quantity in the south of France, by covering copper with the refuse of the grape after the juice has been extracted for making wine: the saccharine matter contained in the husks furnishes acetic acid by fermentation, and in four or six weeks the plates acquire a coating of the acetate. A purer and better article is prepared in this country by covering copper plates with cloth soaked in pyroligneous acid.

Acetate of Oxide of Zinc.—This salt may be prepared by way of double decomposition by mixing sulphate of oxide of zinc with acetate of oxide of lead in equivalent proportions. When made in this way, it is very apt to retain some sulphate of oxide of lead in solution. It is obtained pure by suspending metallic zinc in a dilute solution of acetate of oxide of lead, until all the lead is removed, or by dissolving oxide of zinc in acetic acid. This salt is frequently employed as an astringent collyrium.

Acetate of Protoxide of Mercury.—The only interesting compound of mercury and acetic acid is the acetate of the protoxide, which is sometimes employed in the practice of medicine. It is prepared by mixing crystallized protonitrate of mercury with neutral acetate of potassa in the ratio of one equivalent of each. If both salts are dissolved in a considerable quantity of hot water, the solutions retain their transparency after being mixed; but on cooling, the acetate of protoxide of mercury is deposited in white scales of a silky lustre. It is easily decomposed; and it should be dried by a very gentle heat, and washed with cold water slightly acidulated with acetic acid.

Lactic Acid.

Lactic acid, so named from being first noticed in sour milk, was discovered by Scheele in 1780, has been detected by Berzelius in most of the animal fluids, and in the beet-root by Braconnot, who termed it *nanceic acid.* A suspicion has long existed of its being acetic acid, modified in its character by adhering organic matter; but the recent experiments of J. Gay-Lussac and Pelouze have finally removed all doubt about the existence of lactic acid. (An. de Ch. et de Ph. lii. 410.)

The mode of preparation, employed by J. Gay-Lussac and Pelouze, was to expose a large quantity of the juice of beet-root to a temperature of 80° for several days in order to establish a brisk fermentation, and set it at rest for some weeks until the fermentation has ceased. The liquid is then evaporated to the consistence of syrup, the lactic acid taken up in alcohol, which separates a large quantity of vegetable matter, and the alcoholic extract, redissolved in water, is neutralized by carbonate of oxide of zinc, by which means additional impurities are precipitated. The soluble lactate of oxide of zinc is obtained in crystals by evaporation, is then boiled with animal charcoal freed from phosphate of lime, filtered while hot, and again crystallized. The salt is then perfectly white. The oxide of zinc is thrown down by pure baryta, and the lactate of baryta decomposed by sulphuric acid. If any portions of the acid are not quite white, they may be converted into lactate of lime, purified by animal charcoal, crystallized, dissolved in alcohol, and lastly decomposed by oxalic acid. A similar process applied to milk after long fermentation gives pure lactic acid; and the same acid has been extracted from rice and from nux vomica.

When a solution of lactic acid is concentrated in vacuo with sulphuric acid, it acquires the consistence of syrup, has a density of 1.215, is colourless and inodorous, and has an extremely acid taste. It attracts moisture on exposure to the air, dissolves in all proportions in water and alcohol, and is soluble though to a less degree in ether. When mixed with a strong solution of acetate of potassa, acetic acid is disengaged, and with a strong solution of the acetates of magnesia and oxide of zinc, the lactates of those bases subside. It yields no precipitate with baryta, strontia, or lime.

When the syrupy lactic acid is gradually heated, it becomes coloured and yields inflammable gases, acetic acid, a white crystalline sublimate, and a residue of charcoal. The sublimed matter, freed from adhering moisture by bibulous paper, dissolves freely in boiling alcohol, and separates on cooling in white rhomboidal tables. These crystals fuse at 225°, and the liquid boils at 472°, yielding an inflammable irritating white vapour, which crystallizes as it condenses: it may be volatilized repeatedly without the least decomposition. This sublimed acid, as stated at page 497, differs from the liquid lactic acid in containing two eq. less of water; and though when first put into water the crystals dissolve slowly, yet when once in solution they possess all the characters of the liquid acid.

Lactic acid in uniting with metallic oxides carries into the salt one eq. of water or its elements, which cannot be expelled without decomposing the salt itself. The neutral lactates of protoxides in their dryest state, and exclusive of water of crystallization, consist of one eq. of the oxide and 81.72 parts or one eq. of the acid, the general formula being $\dot{M}+C^{6}H^{5}O^{5}$ or $\dot{M}+\overline{L}$. None of the lactates hitherto examined are insoluble in water. The lactates of baryta, strontia, potassa, soda, ammonia, alumina, and oxide of lead are very soluble, and crystallize with difficulty. That of oxide of silver is white and crystallizes in needles. The salt of zinc is sparingly soluble in cold water, and crystallizes from its hot solution in four-sided prisms, which are insoluble in alcohol, and contain four eq. of water of crystallization. The lactate of magnesia also crystallizes readily, and also with four eq. of water.

Kinic Acid.

This acid, noticed in 1790 by Hofmann, and studied in 1806 by Vauquelin, exists in cinchona bark in combination with lime, quinia, and cinchonia. On evaporating an infusion of bark to the consistence of an extract, and treating the residue with alcohol, a viscid matter remains, consisting of kinate of lime and mucilaginous matters. On dissolving it in water, and allowing the concentrated solution to evaporate spontaneously in a warm place, the kinate crystallizes in rhombic prisms with dihedral summits, and sometimes in rhomboidal plates. From a solution of this salt, exactly decomposed by oxalic acid, kinic acid separates in foliated crystals by evaporation in a warm atmosphere (An. de Ch. lix.). This acid and its combinations have been studied by Henry and Plisson, Liebig, and Baup. (An. de Ch. et de Ph. xli. 325, xlvii. 191, and li. 56). Baup recommends that the acid should be prepared from kinate of lime by means of sulphuric acid.

Kinic acid possesses strong acidity, dissolves in 2½ times its weight of water at 48°, and is also soluble in alcohol, but appears to form an ethereal compound with it. The crystals have a density of 1.637, and consist of 181.8 parts or one eq. of the anhydrous acid, and 9 parts or one eq. of water. When strongly heated it yields a volatile acid called *pyrokinic acid.*

Kinic acid forms very soluble compounds with the alkalies, alkaline earths, and oxides of mercury, lead, and silver. These neutral kinates are so constituted that one eq. of a protoxide is united with 181.8 parts or one eq. of kinic acid, the general formula of these salts being $M+C^{18}H^{10}O^{10}$ or $\dot{M}+\overline{K}$. The rhombic crystals of kinate of lime contain ten eq. of water. Kinate of soda crystallizes in very fine six-sided prisms with four eq. of water; that of strontia in efflorescent prisms or tables with ten eq. of water; and that of baryta with six eq. of water. Kinate of oxide of silver yields by evaporation a white anhydrous salt. The oxides of copper and lead form with it neutral and sub-salts.

Malic Acid.

This acid is contained in most of the acidulous fruits, being frequently associated with tartaric and citric acids. Grapes, currants, gooseberries, and oranges contain it. Vauquelin found it in the tamarind, mixed with tartaric and citric acids, and in the house-leek (*sempervivum tectorum*), combined with lime. It is contained in considerable quantity in apples, a circumstance to which it owes its name. It is almost the sole acidifying principle of the berries of the service-tree (*sorbus aucuparia*), in which it was detected by Mr. Donovan, and described by him under the name of *sorbic acid* in the Philosophical Transactions for 1815; but it was afterwards identified with the malic acid by Braconnot and Houton-Labillardière. (An. de Ch. et de Ph. viii.)

Malic acid may be formed by digesting sugar with three times its weight of nitric acid; but the best mode of procuring it is from the berries of the service-tree. The juice of the unripe berries is diluted with three or four parts of water, filtered, and heated; and while boiling, a solution of acetate of oxide of lead is added as long as any turbidity appears; when the colouring matter of the berry is precipitated, while the malate of that oxide remains in solution. The liquid, while at a boiling temperature, is then filtered. At first a small quantity of dark-coloured salt subsides; but on decanting the hot solution into another vessel, the malate of oxide of lead is gradually deposited, in cooling, in groups of brilliant white crystals. The malate is then decomposed by a quantity of dilute sulphuric acid, insufficient for combining with all the oxide of lead; by which means a solution is procured containing malic acid together with a little lead. The latter is afterwards precipitated by hydrosulphuric acid. The colouring matter is more easily separated if the juice is allowed to ferment for a few days before being used. Another process has been minutely described by Liebig, in order to ensure the absence of citric and tartaric acids with which it is sometimes associated. (An. de Ch. et de Ph. lii. 434.)

Malic acid possesses strong acidity, and a pleasant flavour when diluted. It crystallizes with difficulty, attracts moisture from the air, and is very soluble in water and alcohol. Its aqueous solution is decomposed by keeping, and it is converted into the oxalic by digestion in strong nitric acid. Heated in close vessels it yields a volatile acid called *pyromalic*, the properties of which are not yet known. From the late analysis of Liebig it seems that malic and citric acids are isomeric.

Most of the salts of malic acid are more or less soluble in water. The malates of soda and potassa are deliquescent. The bimalate of ammonia crystallizes very readily. The most insoluble of the malates are those of baryta, lime, and the oxides of lead and silver; but these, excepting the first, are freely soluble in boiling water. These salts are composed of one eq. of base and 58.48 parts or one eq. of acid, the general formula being $\dot{M}+C^4H^2O^4$, or $\dot{M}+\overline{M}$. Pure malate of oxide of lead crystallizes in cooling from its hot solution in small brilliant scales of extreme whiteness. The silver salt also crystallizes from its solution in boiling water; but the liquid darkens from the reduction of oxide of silver.

Citric Acid.

This acid is contained in many of the acidulous fruits, but exists in large quantity in the juice of the lime and lemon, from which it is procured by a process very similar to that described for preparing tartaric acid. To any quantity of lime or lemon juice, finely powdered chalk is added as long as effervescence ensues; and the insoluble citrate of lime, after being well washed with water, is decomposed by digestion in dilute sulphuric acid. The insoluble sulphate of lime is separated by a filter, and the citric acid obtained in crystals by evaporation. They are rendered quite pure by being dissolved in water and recrystallized. The proportions required in this process are 86.98 parts or one eq. of dry citrate of lime, and 49.1 parts or one eq. of strong sulphuric acid, which should be diluted with about 10 parts of water.

Citric acid crystallizes in cooling from a hot saturated solution in crystals which consists of 58.48 parts or one eq. of the anhydrous acid, and 9 parts or one eq. of water, their formula being $\dot{H}+\overline{C}$. These crystals fuse in their water at a heat a little higher than 212°, but without loss of weight. By spontaneous evaporation it crystallizes in large transparent rhomboidal prisms, which differ from the former in composition, their formula being $4\dot{H}+3\overline{C}$: they undergo no change in the air at common temperatures; but at 82° they effloresce and part with exactly half their water, retaining the remainder until the heat is so high that the acid itself is destroyed.

Citric acid has a strong sour taste, with an agreeable flavour when diluted, reddens litmus paper, and neutralizes alkalies. In a dry state it may be preserved for any length of time, but the aqueous solution is gradually decomposed by keeping. The crystals are soluble in an equal weight of cold and in half their weight of boiling water, and are also dissolved by alcohol. It is converted into the oxalic by digestion in nitric acid.

Citric acid is characterized by its flavour, by the form of its crystals, and by forming an insoluble salt with lime, and a deliquescent soluble one with potassa. It does not render lime-water turbid unless the latter is in excess, and fully saturated with lime in the cold.

Citric acid is employed in calico-printing, and in medicinal and domestic purposes instead of lemon juice. Tartaric acid is often substituted for it, as being similar in flavour, and less expensive.

Of the citrates, those of potassa, soda, ammonia, magnesia, and oxides of iron are soluble in water; while those of lime, baryta, strontia, and the oxides of lead, mercury, and silver are very sparingly soluble in hot water, though dissolved by excess of their own acid. They are decomposed by sulphuric acid. No general rule can be stated in respect of their constitution, since, from late observations of Berzelius (An de Ch. et de Ph. liii. 424), it appears that citric acid exhibits very unusual modes of combination, and is prone to form sub-salts of a complex composition. Thus, on mixing neutral citrate of potassa with acetate or nitrate of oxide of lead, it is impracticable to procure the neutral citrate, $\dot{Pb}+\overline{C}$, because it falls in mixture with another salt, the formula of which is $\dot{Pb}^2\overline{C}+2H$, and which, digested with very dilute ammonia, abandoned its water and half of its acid forming the salt $4\dot{Pb}+3\overline{C}$. He obtained the neutral citrate in the purest state by adding an alcoholic solution of citric acid to a solution of acetate of oxide of lead, and hing the precipitate with alcohol; for water deprives it of acid, and it into a sub-salt. On digesting the neutral citrate with acetate of oxide of lead, he obtained a dicitrate, of which the formula is $2\dot{Pb}+\overline{C}$. He found it very difficult to obtain neutral citrates of lime or baryta, as they both resolve themselves readily into acid and sub-salts of complex composition. The most uniform of the citrates is that of oxide of silver, the neutral citrate, $\dot{A}g+\overline{C}$, being readily obtained by double decomposition.

Pyrocitric Acid.—When the crystals of citric acid are subjected to destructive distillation, three volatile products are obtained, namely, a peculiar acid called pyrocitric, water, and a spirituous matter which has not been examined. Pyrocitric acid forms a sparingly soluble salt with oxide of lead; but the pyrocitrates generally have not yet been studied. It appears to form a hydrate with one equivalent of water.

Tartaric Acid.

This acid exists in the juice of several acidulous fruits, but it is almost always in combination with lime or potassa. It is prepared by mixing cream of tartar and chalk in the ratio of their equivalents, 189.11 to 50.62, and boiling them in 10 times their weight of water for about half an hour. The carbonic acid of the chalk is displaced with effervescence, one eq. of insoluble tartrate of lime subsides, and one eq. of neutral tartrate of potassa remains in solution. On washing the former, and then digesting it, diffused through a moderate portion of water, with one equivalent of sulphuric acid, the tartaric acid is set free; and after being separated from the sulphate of lime by a filter, it may be procured by evaporation in prismatic crystals, the primary form of which is a right rhombic prism.

Tartaric acid has a sour taste, which is very agreeable when diluted with water. It reddens litmus paper strongly, and forms with alkalies neutral salts, to which the name of *tartrates* is applied. It requires five or six times its weight of water at 60° for solution, and is much more soluble in boiling water. It is dissolved likewise, though less freely, in alcohol. The aqueous solution is gradually decomposed by keeping, and a similar change is experienced, under the same circumstances, by most of the tartrates. The crystals may be exposed to the air without change. They are converted into the oxalic by digestion in nitric acid.

Tartaric acid cannot be deprived of its water of crystallization, except by uniting with an alkaline base: on attempting to expel it by heat the acid fuses, and is decomposed, yielding, if air is excluded, the usual products of destructive distillation, together with a distinct acid, to which the term pyrotartaric acid is applied. A large residue of charcoal is obtained.

Tartaric acid is distinguished from other acids by forming a white precipitate, bitartrate of potassa, when mixed with any of the salts of that alkali. This acid, therefore, separates potassa from other acids. It occasions with lime-water a white precipitate, which is very soluble in an excess of the acid.

Tartaric acid is remarkable for its tendency to form double salts, the properties of which are often more interesting than the simple salts. The most important of these double salts, and the only ones which have been much studied, are those of potassa and soda, and of oxide of antimony and potassa. The neutral tartrates of the alkalies, of magnesia, and protoxide of copper, are soluble in water; but most of the tartrates of the other bases, and especially those of lime, baryta, strontia, and oxide of lead, are insoluble. All these neutral tartrates, however, which are insoluble in pure water, are soluble in an excess of their acid. They are decomposed by digestion in carbonate of potassa; and when an acid is added in excess, the bitartrate of potassa is precipitated. All the insoluble tartrates are easily procured from neutral tartrate of potassa by way of double decomposition. The neutral tartrates of protoxides consist of 66.48 parts or one eq. of the acid, and one eq. of base, so that the general formula is $\dot{M}+C^4H^4O^5$, or $\dot{M}+\overline{T}$.

Tartrates of Potassa.—The ***neutral tartrate***, frequently called ***soluble tar-***

tar, is formed by neutralizing a solution of the bitartrate with carbonate of potassa: and it is a product of the operation above described for making tartaric acid. Its primary form is a right rhomboidal prism; but it often occurs in irregular six-sided prisms with dihedral summits. Its crystals are very soluble in water, and attract moisture when exposed to the air. They consist of 113.63 parts or one eq. of the neutral tartrate, and 18 or two eq. of water. They are rendered quite anhydrous by a temperature not exceeding 248° F.

Of the *bitartrate* an impure form, commonly known by the name of *tartar*, is found encrusted on the sides and bottom of wine casks, a source from which all the tartar of commerce is derived. This salt exists in the juice of the grape, and, owing to its insolubility in alcohol, is gradually deposited during the vinous fermentation. In its crude state it is coloured by the wine from which it was procured; but when purified, it is quite white, and in this state constitutes the *cream of tartar* of the shops.

Bitartrate of potassa is very sparingly soluble in water, requiring 60 parts of cold and 14 of boiling water for solution, and is deposited from the latter on cooling in small crystalline grains. Its crystals are commonly irregular six-sided prisms, terminated at each extremity by six surfaces; and its primary form is either a right rectangular, or a right rhombic prism. It has a sour taste, and distinct acid reaction. It consists of 47.15 parts or one eq. of potassa, 132.96 or two eq. of acid, and 9 parts or one equivalent of water. Its water of crystallization cannot be expelled without decomposing the salt itself.

Bitartrate of potassa is employed in the formation of tartaric acid and all the tartrates. It is likewise used in preparing pure carbonate of potassa. When exposed to a strong heat, it yields an acrid empyreumatic oil, some pyrotartaric acid, together with water, carburetted hydrogen, carbonic oxide, and carbonic acid, the last of which combines with the potassa. The fixed products are carbonate of potassa and charcoal, which may be separated from each other by solution and filtration. When deflagrated with half its weight of nitre, by which part of the charcoal is consumed, it forms *black flux;* and when an equal weight of nitre is used, so as to oxidize all the carbon of the tartaric acid, a pure carbonate of potassa, called *white flux*, is procured.

Tartrate of Potassa and Soda.—This double salt, which has been long employed in medicine under the name of *Siegnette* or *Rochelle salt*, is prepared by neutralizing bitartrate of potassa with carbonate of soda. By evaporation it yields prismatic crystals, the sides of which often amount to ten or twelve in number; but the primary form, as obtained by cleavage, is a right rhombic prism. (Brooke.) The crystals are soluble in five parts of cold and in a smaller quantity of boiling water, and are composed of 113.63 parts or one eq. of tartrate of potassa, 97.78 parts or one eq. of tartrate of soda, and 72 or eight equivalents of water.

Tartrate of Soda is frequently used as an effervescing draught, by dissolving equal weights of tartaric acid and bicarbonate of soda in separate portions of water, and then mixing the solutions. Soda is better adapted for this purpose than potassa, because the former has little or no tendency to form an insoluble bitartrate.

Tartrate of Oxide of Antimony and Potassa.—This compound, long celebrated as a medicinal preparation under the name of *tartar emetic*, is made by boiling sesquioxide of antimony with a solution of bitartrate of potassa. The oxide of antimony is furnished for this purpose in various ways. Sometimes the *glass* or *crocus* of that metal is employed. The Edinburgh college prepare an oxide by deflagrating sulphuret of antimony with an equal weight of nitre; and the college of Dublin employ the oxy-chloride. Mr. Phillips recommends that 100 parts of metallic antimony in fine powder should be boiled to dryness in an iron vessel with 200 of sulphuric acid, and that the residual subsulphate, after washing with water, be boiled with an equal weight of cream of tartar. The solution of the double salt, however made, should be concentrated by evaporation, and allowed to cool in order that crystals may form.

Tartar emetic yields crystals, which are transparent when first formed, but become white and opaque by exposure to the air. Its primary form has been correctly described by Mr. Brooke as an octohedron with a rhombic base (An. of Phil. N. S. vi. 40.); but the edges of the base are frequently replaced by planes which communicate a prismatic form, and its summits are generally formed with an edge instead of a solid angle, which edge is frequently truncated, presenting a narrow rectangular surface. It frequently occurs in segments, having the outline of a triangular prism, a form which has deceived many into the belief, that the tetrahedron or regular octohedron is the primary form of tartar emetic. It has a styptic metallic taste, reddens litmus paper slightly, and is soluble in 15 parts of water at 60°, and in 3 of boiling water. Its aqueous solution, like that of all the tartrates, undergoes spontaneous decomposition by keeping; and therefore, if kept in the liquid form, alcohol should be added in order to preserve it. From the analysis of Thomson, Phillips, and Wallquist, it may be considered a compound of

	1 eq. Base.	1 eq. Acid.	Equiv.	Formulæ.
Tartrate of sesquioxide of antimony	153.2	+66.48	=219.68	$\underline{\dddot{Sb}}+\overline{T}$.
Tartrate of potassa . .	47.15	+66.48	=113.63	$\dot{K}+\overline{T}$.
Water of crystallization, 2 eq. . . .			= 18	
			351.31	$\left\{ (\dot{K}\overline{T}+\underline{\dddot{Sb}}\overline{T}) + 2\dot{H}. \right.$

Tartar emetic is decomposed by many reagents. Thus alkaline substances, from their superior attraction for tartaric acid, separate the oxide of antimony. The pure alkalies, indeed, and especially potassa and soda, precipitate it imperfectly, owing to their tendency to unite with and dissolve the oxide; but the alkaline carbonates throw down the oxide much more completely. Lime-water occasions a white precipitate, which is a mixture of oxide, or tartrate of the oxide, and tartrate of lime. The stronger acids, such as the sulphuric, nitric, and hydrochloric, cause a white precipitate, consisting of bitartrate of potassa and a subsalt of the oxide of antimony. Decomposition is likewise effected by several metallic salts, the bases of which yield insoluble compounds with tartaric acid. Hydrosulphuric acid throws down the orange sesquisulphuret of antimony. It is precipitated by many vegetable substances, especially by an infusion of gall-nuts, and other similar astringent solutions, with which it forms a dirty white precipitate, which is a tannate of sesquioxide of antimony. This combination is inert, and, therefore, a decoction of cinchona bark is recommended as an antidote to tartar emetic. Heated before the blowpipe, metallic antimony is readily brought into view; and if decomposed by heat in close vessels, a very inflammable pyrophorus is formed.

Racemic Acid.

(*Traubensäure, or Acid of Grapes of the Germans.*)

This acid was first noticed by Mr. Kestner, chemical manufacturer at Thann in the Upper Rhine, who met with it in the preparation of tartaric acid, with which it is associated in the juice of the grape. Kestner, perceiving it to be different from tartaric acid, considered it to be the oxalic: John in 1819 declared it to be distinct from both of those acids, and termed it *acid of the Vosges;* and in 1826 Gay-Lussac and Walchner, receiving a supply from Kestner, made a careful examination of its principal characters. (Jour. de Ch. Med. ii. 335, and Gmelin's Handbuch, ii. 53.) An account of its properties has since been given by Berzelius, who has suggested for it the name of *paratartaric acid*. (An. de Ch. et de Ph. xlvi. 128.)

Racemic acid is associated with tartaric acid, apparently as a biracemate of potassa, in the grape of the Upper Rhine, and subsides during the fermentation of the juice along with cream of tartar: it is probably contained in the juice of all grapes. It is readily obtained by neutralizing the cream of tartar of that district with carbonate of soda, separating the double tartrate of potassa and soda by crystallization, throwing down the racemic acid by a salt of lime or oxide of lead, and decomposing the precipitate by dilute sulphuric acid. On concentrating the solution, the racemic acid crystallizes, and is thus completely separable from any remaining tartaric acid, the latter being much more soluble in water than the former.

The racemic and tartaric acids, besides being associated in nature, afford a most interesting instance of isomerism. Gay-Lussac showed that the equivalents of these acids are represented by the same number; and Berzelius has not only confirmed this fact, but proved that their composition is likewise identical. There is also a close analogy in their chemical relations:—each forms insoluble salts with the same bases, as with lime, baryta, and oxide of lead; biracemate of potassa is a sparingly soluble salt analogous to cream of tartar; and with sesquioxide of antimony the biracemate of potassa yields a double salt, similar in many respects to tartar emetic, though different in the form of its crystals. Nevertheless, the two acids are essentially distinct. The racemic is much less soluble than tartaric acid; the form of its crystals is different, being an oblique rhombic prism; it contains two equivalents of water of crystallization, one of which is given out at 212°, and the other when it unites with alkalies; and it does not *yield* a double salt with potassa and soda. The racemate of lime, too, is less soluble than the tartrate, and is but sparingly dissolved by excess of its acid: a solution of gypsum is not affected by tartaric acid, whereas a little racemic acid after an interval of about an hour causes turbidity: racemate of lime dissolved in dilute hydrochloric acid is almost immediately thrown down by the addition of ammonia; while tartrate of lime under the same treatment does not subside so as to cause turbidity, but after a time slowly separates in octohedral crystals with a square base, which are found adhering to the sides of the glass. It thus appears that racemic and tartaric acids have the same atomic weight, the same composition, and in several respects the same chemical properties; and yet on closely investigating *all* their characters, they are found to be essentially distinct. Moreover, the different arrangement of the atoms in these two acids is indicated by the different form of similar combinations.

Benzoic Acid.

Benzoic acid exists in gum benzoin, in storax, in the balsams of Peru and Tolu, and in several other vegetable substances. M. Vogel has detected it in the flowers of the *trifolium melilotus officinalis*. It is found in considerable quantity in the urine of the cow and other herbivorous animals, and is perhaps derived from the grasses on which they feed. It has also been detected in the urine of children.

This acid is commonly extracted from gum benzoin. One method consists in heating the benzoin in an earthen pot, over which is placed a cone of paper to receive the acid as it sublimes; but since the product is always impure, owing to the presence of empyreumatic oil, it is better to extract the acid by means of an alkali. The usual process consists in boiling finely powdered gum benzoin in a large quantity of water along with lime or carbonate of potassa, by which means a benzoate is formed. To the solution, after being filtered and concentrated by evaporation, hydrochloric acid is added, which unites with the base, and throws down the benzoic acid. It is then dried by a gentle heat, and purified by sublimation.

Benzoic acid has a sweet and aromatic rather than a sour taste; but it reddens litmus paper, and neutralizes alkalies. It fuses readily by heat, and at a temperature a little above its point of fusion, it is converted into vapour, emitting a peculiar, fragrant, and highly characteristic odour, and condensing on cool surfaces without change. When strongly heated it takes fire, and burns with a clear yellow flame. It undergoes no change by exposure to the air, and is not decomposed by the action even of nitric acid. It requires about 24 parts of boiling water for solution, and nearly the whole of it is deposited on cooling in the form of minute acicular crystals of a silky lustre. It is very soluble in alcohol, especially by the aid of heat.

Agreeably to the late admirable researches of Liebig and Wöhler on the oil of bitter almonds, benzoic acid must be regarded as the oxide of a compound inflammable body which will be treated of in the third section, and to which they have applied the name of *benzule*, composed of *benz*, and *ὑλη matter* or *principle*. Benzule is composed of 85.68 parts or fourteen eq. of carbon, 5 parts or five eq. of hydrogen, and 16 parts or two eq. of oxygen, its equivalent being 106.68. The composition of benzoic acid may be thus stated, an equivalent being represented by Bz:—(An. de Ch. et de Ph. li. 273.)

Anhydrous benzoic acid. Benzule 106.68+Oxygen 8=114.68 $Bz+O$ or $\dot{B}z$.

The crystallized acid contains one eq. of water, its formula being $\dot{B}z+\dot{H}$, and it cannot be deprived of its water by heat. Its water of crystallization is also contained in benzoate of oxide of lead, $\dot{P}b\dot{B}z+\dot{H}$, and is not expelled by heat until the salt itself is decomposed. Benzoate of oxide of silver is anhydrous, its formula being $\dot{A}g+\dot{B}z$: it falls as a white powder when nitrate of oxide of silver is mixed in solution with benzoate of ammonia, is completely dissolved by boiling water, and is deposited on cooling in brilliant foliated crystals.

The composition of neutral benzoates of protoxides is represented by the general formula $\dot{M}+\dot{B}z$. Most of these are soluble in water; the most insoluble are the benzoates of the oxides of lead, mercury, and silver, and peroxide of iron.

Meconic Acid.

This acid, which derives its name from Μηκων, *poppy*, has hitherto been found only in opium, where it exists in combination with morphia; and it is best prepared from the mixed sulphate and meconate of lime obtained in Gregory's process for hydrochlorate of morphia. The impure meconate of lime is put into ten times its weight of water at 200°, and hydrochloric acid is added until the meconate is dissolved: the solution is then filtered, and on cooling deposites bimeconate of lime in the form of light white scaly or acicular crystals. These are again dissolved by hot dilute hydrochloric acid as before, in order to separate the remainder of the lime; and on cooling crystals of meconic acid subside. If they leave a residue after calcination, they should be again dissolved in acid and re-crystallized. To procure the acid quite white, it is saturated with potassa diluted with the smallest quantity of water required by the aid of heat to dissolve the meconate, and when cold the fluid part, which retains the colouring matter, is separated from the crystals by filtration and pressure in cloth or bibulous paper. The meconate of potassa is then decomposed in the same way as the meconate of lime, when meconic acid is obtained perfectly white and in transparent micaceous scales.

Meconic acid has an acid taste and reaction, and is soluble both in alcohol and water, requiring only four times its weight of boiling water for solution. The crystals are unchanged in the air, but when heated to 212° they become quite opaque and lose 21.5 per cent. of water of crystallization, being 27 parts or three eq. to 100.84 parts or one eq. of the anhydrous acid. They still continue meconic acid even when heated to 248°; but if boiled in water carbonic acid gas is disengaged, the liquid becomes brown, meconic acid disappears, and metameconic acid is generated.

Meconic acid is remarkable for forming with persalts of iron a purple-red colour, which affords a good test for the acid whether free or combined, and detects meconic acid in solutions of opium, when the morphia combined with it could not be discovered; the colour is very like that produced by hydrosulphocyanic acid. Meconic acid forms insoluble white salts with lime, baryta, and the oxides of lead and silver, which are soluble in nitric acid. It is very prone to form bisalts, as the bimeconate of potassa and lime, which are of sparing solubility. The meconate of oxide of silver consists of 116 parts or one eq. of that base and 100.84 parts or one eq. of meconic acid, its formula being $\dot{A}g+C^7H^2O^7$. The neutral meconates of protoxides are analogous in composition.

Metameconic Acid.

Robiquet, who has described the preparation and properties of meconic acid, also observed its conversion into metameconic acid by boiling its aqueous solution; and Liebig, by his skilful analysis of both acids, has proved (An. de Ch. et de Ph. li. 241 and liv. 26) that

$$\left.\begin{array}{l}\text{2 eq. of meconic acid}\\ \quad 2(7C+2H+7O)\end{array}\right\}\text{yield}\left\{\begin{array}{ll}\text{1 eq. of metameconic acid} & 12C+4H+10O\\ \text{and 2 eq. carbonic acid} & \quad 2(C+2O).\end{array}\right.$$

The brown matter formed when a solution of meconic acid is boiled, and which adheres to the acid, does not seem essential to the change, since it takes place in a very slight degree when a meconate is boiled with hydrochloric acid, the resulting metameconic acid being then nearly colourless.

Metameconic acid is soluble in 16 times its weight of boiling water, and separates on cooling in anhydrous hard crystalline grains, wholly different from meconic acid. It reddens persalts of iron, but its other properties have not yet been studied.

When anhydrous meconic acid is distilled, it yields among other products a crystalline sublimate, which till lately was regarded as pure meconic acid, though in reality it is not so. It reddens persalts of iron; but whether it is metameconic acid, or some other compound, has not been determined.

Tannic Acid (Tannin.)

This substance exists in an impure state in the excrescences of several species of oak, called gall-nuts; in the bark of most trees; in some inspissated juices, such as kino and catechu; in the leaves of the tea-plant, sumach, and whortleberry (uva ursa), and in astringent plants generally, being the chief cause of the astringency of vegetable matter. It is frequently associated with gallic acid, as in gall-nuts, in most kinds of bark, and in tea; but in kino, catechu, and cinchona bark, little or no gallic acid is present.

Several processes are recommended for the preparation of tannic acid. Thus, it may be precipitated from a solution of gall-nuts by chloride of tin, and the precipitate after washing be decomposed by hydrosulphuric acid; or it may be thrown down by concentrated sulphuric acid in the cold, and the precipitate, when dried in folds of bibulous paper, be decomposed by digestion with carbonate of oxide of lead. But in these and similar processes the tannic acid, which is very prone to change, is more or less modified in its character; and, therefore, the process with ether lately recommended by Pelouze is preferable. (An. de Ch. et de Ph. liv. 337.) The lower aperture of an elongated narrow glass vessel is loosely closed by a piece of linen; on this is laid some gall-nuts in fine powder, which is gently pressed together, and then sulphuric ether is poured upon the powder: the upper aperture is closed by a stopper to prevent loss of ether by evaporation, and the apparatus fixed in the mouth of a bottle, which receives the ether as it slowly percolates through the powder. It appears that the small quantity of water contained in ether as sold in the shops, combines with tannic acid to the exclusion of the other ingredients of the gall-nuts, and forms a saturated aqueous solution, which collects as a distinct stratum below the ether. After exhausting the gall-nuts by repeated portions of ether, the ethereal part is drawn off and purified by distillation, and the aqueous solution of tannic acid, after being washed with ether, is evaporated to dryness at a very gentle heat or in vacuo with sulphuric acid. The tannic acid is left as a uniform spongy mass, not crystallized, either quite white or with a slightly yellow tint. Its quantity varies from 35 to 40 per cent. of the gall-nuts employed.

Pure tannic acid is colourless and inodorous, has a purely astringent taste without bitterness, and may be preserved without change in the solid state. It is very soluble in water, and the solution reddens litmus, and decomposes alkaline carbonates with effervescence, thus leaving no doubt of its acidity. Alcohol and ether also dissolve tannic acid, but more sparingly than water, especially when anhydrous. Solutions of tannic acid do not affect pure protosalts of iron, but strike a deep blue precipitate with the persalts: a strong solution of it yields a copious white precipitate with the sulphuric, nitric, hydrochloric, phosphoric, and arsenic acids, but none with the oxalic, tartaric, lactic, acetic, citric, succinic, and selenious acids. It is precipitated also by the carbonates of potassa and ammonia, by the alkaline earths, alumina, and many solutions of the second class of metals. With cinchonia, quinia, brucia, strychnia, codeia, narcotina, and morphia, it yields white tannates, which are sparingly soluble in pure water, but are dissolved readily by acetic acid. By digestion with nitric acid it yields oxalic acid.

A solution of tannic acid may be preserved without change, provided it be excluded from oxygen gas; but in open vessels it gradually absorbs oxygen, an equal volume of carbonic acid is evolved, it becomes turbid, and deposites a crystalline matter of a gray colour, nearly all of which is gallic acid. After digestion with a little animal charcoal, the gallic acid is perfectly white and pure. There is no doubt, therefore, of the conversion of tannic into gallic acid.

Tannic acid is distinguished from all substances, except gallic acid, by forming a deep blue precipitate with persalts of iron, which is the basis of writing-ink and the black dyes; and from gallic acid, by yielding with a solution of gelatin a white flaky precipitate, which is soluble in a solution of gelatin, but insoluble in water and gallic acid. This substance, to which the name of *tanno-gelatin* has been applied, is the basis of leather, being always formed when skins are macerated in an infusion of bark. When dried it becomes hard and tough, and resists putrefaction. Its composition is apt to vary, according to the relative quantities of the materials used in its formation; but if the gelatin is in slight excess only, the resulting compound contains 54 per cent. of tannic acid. This acid cannot be so wholly separated by gelatin, that the remaining solution shall not be affected by a persalt of iron; but Pelouze finds that every trace of it is removed by a piece of skin previously cleansed by lime as in the manufacture of leather, leaving any gallic acid which may have been present.

From the experiments of Davy, it appears that the inner cortical layers of bark are the richest in tannic acid. Its quantity is greatest in early spring when the buds begin to open, and smallest during winter. Of all the varieties of bark which he examined, that of the oak contains the largest quantity of tannic acid.

Tannic acid dried at 240° is anhydrous, such as it exists in the white tannate of oxide of lead when dried at 248°. Pelouze found this salt to consist of 111.6 parts or one eq. of protoxide of lead, and 215.16 parts or one eq. of tannic acid, its formula being $\dot{\mathrm{Pb}}+\overline{\mathrm{Tn}}$. The other tannates of protoxides have most probably a similar composition. The white tannate of sesquioxide of antimony and the blue tannate of peroxide of iron are thus constituted:—

	Base.	Acid.	Equiv.	Formulæ.
Tannate of sesquiox. of antimony	153.2	+ 645.48	= 798.68	$\underline{\dddot{\mathrm{Sb}}}+3\overline{\mathrm{Tn}}$.
Tannate of peroxide of iron .	80	+ 645.48	= 725.48	$\underline{\dddot{\mathrm{Fe}}}+3\overline{\mathrm{Tn}}$.

The various kinds of tannic acid obtained from cinchona bark, kino, and other sources, correspond in most respects with that above described; but at the same time some difference is observable, some kinds striking a green instead of a deep blue colour with the persalts of iron. The tannic acid from catechu is less highly oxidized than that from gall nuts (page 498).

Artificial Tannic Acid.—This substance was discovered by Mr. Hatchett, and is best prepared by the action of nitric acid on charcoal (Phil. Trans. 1805-6). For this purpose 100 grains of charcoal in fine powder are digested in an ounce of nitric acid, of density 1.4, diluted with two ounces of water, with a gentle heat until the charcoal is dissolved. The reddish-brown solution is then evaporated to dryness, in order to expel the nitric acid, the temperature being carefully regulated towards the close of the process, so that the product may not be decomposed.

Artificial tannic acid is a brown fusible substance of a resinous fracture, astringent taste, and acid reaction. It is soluble even in cold water and in alcohol. With a salt of iron and solution of gelatin it acts precisely in the same manner as natural tannic acid. It differs, however, from that substance in not being decomposed by the action of strong nitric acid.

Artificial tannic acid may be prepared in several ways. Thus it is generated by the action of nitric acid, both on animal or vegetable charcoal, and on pit-coal, asphaltum, jet, indigo, common resin, and several other resinous substances. It is also procured by treating common resin, elemi, assafœtida, camphor, balsams, &c., first with sulphuric acid, and then with alcohol.

Gallic Acid.

This acid, discovered by Scheele in 1786, exists in the bark of many trees, in gall-nuts, and in most substances which contain tannic acid, being probably developed by the oxidation of that acid. The best process for preparing it is that of Scheele as modified by Braconnot (An. de Ch. et de Ph. ix). Any quantity of gall-nuts, reduced to powder, is infused for a few days in four times its weight of water, and the infusion, after being strained through linen, is kept for two months in an open vessel and a moderately warm atmosphere. During this period the surface of the liquid becomes mouldy, and tannic acid is converted by the oxygen of the air into gallic acid, which subsides as a yellowish crystalline matter, mixed with ellagic acid. On evaporating the solution to the consistence of syrup, an additional quantity subsides on cooling. The object of this process is to give an opportunity for the oxidation of tannic acid, which disappears more or less completely, and is the principal source of the gallic acid, since the latter usually exists in gall-nuts in very small quantity. The impure gallic is separated from the insoluble ellagic acid by boiling water; and it is rendered white by digestion with animal charcoal deprived of its phosphate of lime by dilute nitric acid. When the colourless solution is concentrated by evaporation, the gallic acid is deposited in small white acicular crystals of a silky lustre. Some crystals prepared by Mr. Phillips, and examined by Mr. Brooke, were in the form of an oblique rhombic prism.

Pure gallic acid has a weak acid taste, accompanied with slight astringency, and reddens litmus. In boiling water it is freely soluble, but it requires 100 parts of cold water for solution; and it is soluble in ether. Its aqueous solution continues unchanged if protected from oxygen gas; but in open vessels it is gradually decomposed, acquires a yellow tint, and deposites a dark brown matter. With sulphate of the protoxide of iron, it produces scarcely any change; but with the persulphate it gives a dark blue precipitate, which is more soluble than the tannate of that oxide, and slowly dissolves after its formation. When the recent precipitate is boiled in water, the sulphuric acid gradually reunites with the iron, which is reduced to the state of protoxide at the expense of gallic acid, carbonic acid being disengaged. The same action ensues slowly in the cold, and the tannate of the peroxide is liable to a similar change. Both the tannate and gallate of the peroxide exist in ink.

Gallic acid does not precipitate solutions of gelatin, or salts of the vegetable alkalies. With lime-water it gives a brownish-green precipitate, which is redissolved by an excess of the alkali, and acquires a reddish tint, owing it is said to the decomposing agency of the air.

Crystallized gallic acid loses its water at 248°, and then has the same composition (page 497) as the acid when united with oxide of lead. This salt falls as a white precipitate when gallic acid is mixed in solution with the acetate or nitrate of oxide of lead; and Pelouze states that when dried at 248° it consists of 111.6 parts or one eq. of protoxide of lead, and 85.84 parts or one eq. of gallic acid; whence its formula is $\dot{Pb}+C^7H^3O^5$, or $\dot{Pb}+\overline{G}$. The gallates in general have been but little examined; but $\dot{M}+\overline{G}$ may be taken as the general formula of the constitution of neutral gallates of protoxides. The gallates of potassa, soda, and ammonia are soluble in water; but the gallates of most other metallic oxides are insoluble.

Pyrogallic Acid.

Braconnot first noticed that the crystals obtained by subliming gallic acid are not, as was thought, gallic acid, but an acid of a peculiar kind which he has termed the *pyrogallic*, to indicate its igneous origin. Pelouze has confirmed this observation, and finds that if pure anhydrous gallic acid be heated in a dry retort plunged in oil which is kept at a temperature varying from 410° to 419°, it is resolved entirely into carbonic acid which is evolved as gas, and pyrogallic acid which condenses in the upper part of the retort in numerous scaly crystals of brilliant whiteness. The decomposition is such that (An. de Ch. et de Ph. xlvi. 206, and liv. 352.)

$$\text{1 eq. gallic acid } 7C+3H+5O \text{ yields} \left\{ \begin{array}{ll} \text{1 eq. pyrogallic acid} & 6C+3H+3O \\ \text{and 1 eq. carbonic acid} & C+2O. \end{array} \right.$$

Pyrogallic acid has a faintly bitter astringent taste without acidity, and barely reddens litmus paper. At 247° it fuses and at 410° boils, yielding a colourless vapour of a faint odour, somewhat resembling that of benzoic acid. At 480° it blackens, and is resolved into metagallic acid and water,

$$\left. \begin{array}{l} \text{2 eq. pyrogal-} \\ \text{lic acid} \end{array} \right\} 2(6C+3H+3O) \text{ yielding} \left\{ \begin{array}{ll} \text{1 eq. metagal. acid} & 12C+3H+3O \\ \text{and 3 eq. of water} & 3(H+O). \end{array} \right.$$

Pyrogallic acid dissolves in two or three times its weight of cold water, and is very soluble in alcohol and ether. Its aqueous solution, at first colourless, becomes brown by exposure to the air, and in a few days is decomposed. With the nitrates of the oxides of silver and mercury and a persalt of iron, it is decomposed, and reduces the two former oxides to the metallic state, and the latter to the state of protoxide, the iron solution acquiring a brown colour. With a protosalt of iron it strikes a blackish-blue colour, and a similar tint is developed with a persalt of iron and a pyrogallate.

Metagallic Acid.

If instead of decomposing gallic acid at 419°, it is suddenly heated to 480°, carbonic acid and water are disengaged, and instead of a sublimate of pyrogallic acid, a black shining insoluble matter like charcoal remains in the retort, to which Pelouze has given the name of metagallic acid. Its formation obviously depends on the decomposition of pyrogallic acid at the instant of its formation, agreeably to the formula above given. The same products are obtained by distilling tannic acid at 480°, in addition to which pyrogallic acid is formed if the distillation is conducted at 410°.

Metagallic acid is dissolved by the alkalies, forming neutral metagallates, from which it is precipitated in black flakes by acids; and it decomposes alkaline carbonates with effervescence. The metagallate of potassa gives black precipitates with soluble salts of baryta, strontia, *lime*, magnesia, and the oxides of iron, zinc, copper, lead, and silver, showing that the metagallates of those bases are insoluble. The silver salt consists of 116 parts or one eq. of oxide of silver, and 100.44 or one eq. of metagallic acid, its formula being $\dot{A}g+C^{12}H^{3}O^{3}$. The acid as first formed, or as precipitated from its salts by acids, is a hydrate with one eq. of water, of which the formula is $\dot{H}+C^{12}H^{3}O^{3}$.

Ellagic Acid.

This acid, called *ellagic* by Braconnot, from the word *galle* read backwards, is left in the process for gallic acid in the form of a gray powder, insoluble in water, but soluble in a solution of potassa, and precipitated by acids as a yellowish-gray powder. Ellagic acid, when dried at 248°, was found by Pelouze to have the same composition as anhydrous gallic acid, minus one eq. of water; and the acid before being so dried is a hydrate identical in its ingredients with anhydrous gallic acid.

Succinic Acid.

This acid is procured by heating powdered amber in a retort by a regulated temperature, when the succinic acid, which exists ready formed in amber, passes over and condenses in the receiver. As first obtained, it has a yellow colour and peculiar odour, owing to the presence of some empyreumatic oil; but it is rendered quite pure and white by being dissolved in nitric acid, and then evaporated to dryness. The oil is decomposed, and the succinic acid is left unchanged.

Succinic acid has a sour taste, and reddens litmus paper. It is soluble both in water and alcohol, and crystallizes by evaporation in anhydrous prisms. When briskly heated, it fuses, undergoes decomposition, and in part sublimes, emitting a peculiar and very characteristic odour.

The salts of succinic acid have been little examined. The succinates of the alkalies are soluble in water. That of ammonia is frequently employed for separating iron from manganese, persuccinate of iron being quite insoluble in cold water, provided the solutions are neutral. Succinate of protoxide of manganese, on the contrary, is soluble.

By reference to the table (page 497) it will be seen that succinic acid differs in composition from the acetic only in containing one equivalent less of hydrogen.

Mucic or *Saccholactic Acid* was discovered by Scheele in 1780. It is obtained by the action of nitric acid on certain substances, such as gum, manna, and sugar of milk. The readiest and cheapest mode of forming it is by digesting gum with three times its weight of nitric acid. On applying heat, effervescence ensues, and three acids—the oxalic, malic, and saccholactic—are the products. The latter, from its insolubility, subsides as a white powder, and may be separated from the others by washing with cold water. In this state Dr. Prout says it is very impure. To purify it he digests with a slight excess of ammonia, and dissolves the resulting salt in boiling water. It is filtered while hot, and the solution evaporated slowly almost to dryness. The saccholactate of ammonia is thus obtained in crystals, which are to be washed with cold distilled water, until they become quite white. They are then dissolved in boiling water, and the saturated hot solution dropped into cold dilute nitric acid.

The saccholactic is a weak acid, which is insoluble in alcohol, and requires sixty times its weight of boiling water for solution. When heated in a retort it is decomposed; and in addition to the usual products, yields a volatile white substance, to which the name of *pyromucic acid* has been applied.

Camphoric Acid.—This compound has not hitherto been found in any plant, and is procured only by digesting camphor for a considerable time in a large excess of nitric acid. As the solution cools, the camphoric acid separates out in crystals; but it appears from some observations of Liebig (An. de Ch. et de Ph. xlvii. 95), that so long as it retains the odour of camphor, as it is apt to do, its freedom from that substance is incomplete, and it requires renewed digestion with nitric acid. It is sparingly soluble in water, fuses at 145°, and sublimes at a temperature by no means elevated. Its taste is rather bitter, and when quite pure has probably no odour. It reddens litmus paper, and combines with alkaline bases, forming salts which are called camphorates: those with the alkalies are very soluble and even deliquescent, but with oxide of lead it forms an insoluble compound. Camphoric acid is now to be regarded as an oxide of the compound radical, camphene. (Page 256.)

Valerianic Acid.—The existence of this acid was observed by M. Grote, and since studied by Penz and Trommsdorff (An. de Ch. et de Ph. liv. 208.) This acid exists in the root of valerian (*valeriana officinalis*) and passes over along with an essential oil when that root is distilled: on agitating the product with carbonate of magnesia and water, and distilling, the essential oil is expelled, and valerianate of magnesia is left. On decomposing this salt by dilute sulphuric acid, the valerianic acid may be obtained by distillation, partly dissolved in the water which passes over with it, and partly as an oleaginous matter floating on its surface.

Pure valerianic acid is a colourless oleaginous fluid, of density 0.944, an odour like that of valerian, and a strong, acid, disagreeable taste. It boils at 270°, but distils along with aqueous vapour at a much lower temperature: the oily stain which it gives to paper disappears entirely by heat. It burns with a vivid flame without residue. It dissolves in every proportion in alcohol, and in 30 parts of cold water. It has a strong acid reaction, and forms salts with alkaline bases, most of which are soluble in alcohol and water, are fatty to the touch, and when decomposed emit the peculiar odour of the acid. From the analysis of Ittner (page 497) the general formula of the neutral valerianates of protoxides is $\dot{M}+C^{10}H^{9}O^{3}$, and the oily acid is a hydrate with one eq. of water.

Rocellic Acid.—This acid was discovered by Heeren in the *rocella tinctoria*, and is separated by acting on the lichen with a solution of ammonia, precipitating with chloride of calcium, and decomposing the rocellate of lime by hydrochloric acid, when rocellic acid subsides. It is purified by solution in ether, and is deposited by evaporation in minute white crystals of a silky lustre. This acid fuses at 266°, is very soluble in alcohol and ether, and is insoluble in water.

Moroxylic Acid.—This compound, which was first discovered by Klaproth, is found in combination with lime on the bark of the *morus alba* or white mulberry, and has hence received the appellation of *moric* or *moroxylic acid.* It is obtained by decomposing moroxylate of lime by acetate of oxide of lead, and then separating that oxide by means of sulphuric acid.

Hydrocyanic or *prussic acid*, which is not an unfrequent production of plants, has already been described.

The *sorbic*, as already mentioned, has been shown to be malic acid.

Rheumic Acid.—This name was applied to the acid principle contained in the stem of the garden rhubarb; but M. Lassaigne has shown it to be oxalic acid.

Chloroxalic Acid.—When crystallizable acetic acid is put into a glass vessel full of dry chlorine, and exposed for a day to bright sunshine, hydrochloric acid gas is generated, and during the night chloroxalic acid is deposited in dendritic crystals or small rhombic scales. In order to obtain it pure the chlorine should be in excess, and the gases subsequently expelled from the flask by dry air. The new acid is very volatile and deliquescent, and when evaporated *in vacuo*, yields rhombic crystals. Its elements are in such proportion that it may be regarded as a compound of one equivalent of hydrochloric and one equivalent of oxalic acid. These observations were made by Dumas. (Pog. Annalen, xx. 166)

Boletic Acid was discovered by M. Braconnot in the juice of the *Boletus pseudo-igniarius*. As it is a compound of little interest, I refer the reader to the original paper for an account of it. (Annals of Phil. vol. ii.)

Igasuric Acid.—Pelletier and Caventou have proposed this name for the acid which occurs in combination with strychnia in the nux vomica and St. Ignatius's bean. It may be conveniently obtained by adding acetate of oxide of lead to the aqueous solution of nux vomica prepared as in the preparation of strychnia, when the igasurate of that oxide subsides: the precipitate, after being washed, is put into water and decomposed by a current of hydrosulphuric acid gas. The solution of igasuric acid is then separated from sulphuret of lead by filtration, and may be purified either by digestion with animal charcoal, from which phosphate of lime has been removed by an acid, or by a second precipitation with acetate of oxide of lead. On concentrating the purified solution to the consistence of thin syrup, and placing it in a warm situation, the acid separates in crystals which are commonly indistinct in their form.

Igasuric acid forms soluble salts with the alkalies, baryta, and the oxides of iron, silver, and mercury. With oxide of lead, lime, and magnesia, it yields sparingly soluble compounds; but the two latter are dissolved by hot water. With sulphate of oxide of copper in neutral solutions, it occasions, either immediately or after a short interval, a light green precipitate, which is very characteristic of igasuric acid.

Suberic Acid is produced by the action of nitric acid on cork. Its acid properties are very feeble. It is very soluble in boiling water, and the greater part of it is deposited from the solution in cooling in the form of a white powder. Its salts, which have been little examined, are known by the name of *suberates*.

Zumic Acid.—This compound, procured by Braconnot from several vegetable substances which had undergone the acetous fermentation, appears from the observations of Vogel to be lactic acid. (Annals of Philosophy, vol. xii.)

Pectic Acid.—This substance, distinguished by its remarkable tendency to gelatinize, a property from which its name is derived (from πηκτις, coagulum), was originally described by Braconnot; and it has since been examined by the late celebrated Vauquelin. (An. de Ch. et de Ph. xxviii. 173, and xli. 46.) Braconnot believed it to be present in all plants; but he extracted it chiefly from the carrot. For this purpose the carrot is made into a pulp, the juice is expressed, and the solid part well washed with distilled water. It is then boiled for about ten minutes with a very dilute solution of pure potassa, or, as Vauquelin advised, with bicarbonate of potassa in the ratio of 5 parts to 100 of the washed pulp, and the chloride of calcium is added to the filtered liquor. The precipitate, consisting of pectic acid and lime, is well washed, and the lime removed by water acidulated with hydrochloric acid.

Pectic acid, as thus procured, is in the form of jelly. It is insoluble in cold water and acids, and nearly so in boiling water. It has a slight acid reaction, and a feeble neutralizing power with alkalies, with which it forms soluble compounds. The earthy pectates are very insoluble, and on this account, in preparing pectic acid, pure water must be used; for the process always fails, when water containing earthy salts is employed.

By digestion in a strong solution of potassa, pectic acid disappears, the liquid becomes brown, and oxalate of potassa is obtained by evaporation. This fact excites some suspicion that pectic acid may be a compound of oxalic acid with a vegetable principle analogous to gum; but the conversion of organic substances in general into oxalic acid by the action of potassa, as already noticed at page 494, diminishes the force of this objection.

Lactucic Acid.—This acid was obtained by Pfaff from the juice of the *lactuca virosa*, who throws down the acid by a salt of copper or lead, and then separates the metallic oxide by hydrosulphuric acid. It is said to differ from oxalic acid, which in most respects it resembles, by giving a green precipitate with the protosalts of iron, and a brown with sulphate of protoxide of copper; but its properties are imperfectly known.

Crameric Acid.—This acid was discovered by M. Peschier of Geneva in the extract of Rhatany root, *Crameria triandra.* After separating from an aqueous solution of the extract all the tannic acid by means of gelatin, and then neutralizing by ammonia, acetate of oxide of lead is added as long as it occasions a precipitate: the cramerate of that oxide is decomposed either by sulphuric acid or hydrosulphuric acid; and the solution is concentrated in order that the crameric acid may crystallize. This acid forms a sparingly soluble salt with baryta; and it is singular that the small quantity which is dissolved, is not precipitated by sulphuric acid, though the baryta may be thrown down by an alkaline carbonate.

Caincic Acid.—This acid, discovered by MM. François, Caventou, and Pelletier, is the bitter principle of the bark of the cainca root, a Brazilian shrub which is employed for the cure of intermittent fever. (Journ. de Pharm. xvi. 465.) It crystallizes in delicate white needles arranged in tufts like hydrochlorate of morphia, has a remarkably bitter taste, and an acid reaction. It is sparingly soluble in water and ether, but is abundantly dissolved by alcohol, especially when heated. It unites with the alkalies forming soluble salts which do not crystallize, and from which acids throw down caincic acid. It forms soluble neutral salts with baryta and lime, but the caincate of oxide of lead and the subcaincate of lime are insoluble in water. It is decomposed by the concentrated mineral acids; and the hydrochloric, even in the cold, converts it into a gelatinous matter which is nearly insipid. Its equivalent has not yet been ascertained; but Liebig finds that the crystallized acid loses 9 per cent. of water at 212°, and that 100 parts of the acid thus dried contain 57.38 parts of carbon, 7.48 of hydrogen, and 35.14 of oxygen.

Caincic acid is prepared by exhausting the bark with hot alcohol, and evaporating the solution to the consistence of an extract, which is then boiled in water, and the hot aqueous solution, after filtration, is decomposed by an excess of lime. The precipitate treated with oxalic acid yields oxalate of lime and free caincic acid, which are both insoluble in cold water. Hot alcohol takes up the latter, which is decolorized by animal charcoal.

Indigotic Acid.—This acid has been studied by Buff, and recently analyzed by Dumas. (An. de Ch. et de Ph. xxxvii. 160, xxxix. 290, li. 174, and liii. 176.) It is generated, with evolution of carbonic acid and binoxide of nitrogen gases in equal measures, but without the production of any carbazotic acid, by boiling indigo in rather dilute nitric acid, formed by mixing nitric acid of sp. gr. 1.2 with an equal weight of water. To the solution, kept boiling, indigo in coarse powder is gradually added, as long as effervescence continues; and hot water is occasionally added to supply loss by evaporation. The impure indigotic acid, deposited in cooling, is boiled with oxide of lead and filtered, in order to separate resin; and the clear yellow solution is decomposed by sulphuric acid, and again filtered at a boiling temperature. On cooling, the acid crystallizes in yellowish-white needles. In order to purify them completely, they were digested in water with carbonate of baryta; and the indigotate of baryta, deposited from the hot filtered solution in cooling, was dissolved in hot water, and decomposed by an acid. Indigotic acid was thus obtained in acicular crystals of snowy whiteness, which contracted greatly in drying, and lost their crystalline aspect; but the dry mass was dazzling white, and had a silky lustre.

Indigotic acid decomposes carbonates, but is a feeble acid, and reddens litmus faintly. It requires 1000 times its weight of cold water for solution, but is soluble to any extent in hot water and alcohol. Heated in a tube it fuses, and sublimes without decomposition; and the fused mass, in cooling, crystallizes in six-sided plates. When heated in open vessels, it is inflamed, and burns with much smoke.

Dumas has compared together the constitution of indigogen, *indigo-blue*, and indigotic acid, and finds that they may be viewed as oxides of the same compound radical: thus

	Carb.	Hyd.	Nitr.	Oxy.	Equiv.	Formulæ.
Indigogen .	275.4	+15	+42.45	+ 32	=364.85	$C^{45}H^{15}N^{2}+4O$.
Indigo-blue .	275.4	+15	+42.45	+ 48	=380.85	$C^{45}H^{15}N^{2}+6O$.
Do. in 100 parts	72.8	+ 4.04	+10.8	+ 12.36		
Indigotic acid	275.4	+15	+42.45	+240	=572.85	$C^{45}H^{15}N^{2}+30O$.
Do. in 100 parts	48.23	+ 2.76	+ 7.73	+ 41.28		

The equivalent of indigotic acid as here represented has not been proved by the composition of its salts, great uncertainty existing as yet respecting the composition of a neutral indigotate.

Carbazotic Acid.—This name has been applied by Liebig to a peculiar acid formed by the action of nitric acid on indigo. It was first noticed by Hausmann, and subsequently examined by Proust, Fourcroy and Vauquelin, Chevreul, and Liebig. It is made by dissolving small fragments of the best indigo in 8 or 10 times their weight of moderately strong nitric acid, and boiling as long as nitrous acid fumes are evolved. During the action, carbonic, hydrocyanic, and nitrous acids are evolved; and in the liquid, besides carbazotic acid, is found a resinous matter, artificial tannin, and indigotic acid. On cooling, carbazotic acid is freely deposited in transparent yellow crystals; and on evaporating the residual liquid, and adding cold water, an additional quantity of the acid is procured. To render it quite pure, it should be dissolved in hot water, and neutralized by carbonate of potassa. As the liquid cools, carbazotate of potassa crystallizes, and may be purified by repeated crystallization. The acid may be precipitated from this salt by sulphuric acid.

Carbazotic acid is sparingly soluble in cold water; but it is *dissolved* much more freely by the aid of heat, and on cooling yields brilliant crystalline plates of a yellow colour. Ether and alcohol dissolve it readily. It is fused and volatilized by heat without decomposition; but when suddenly exposed to a strong heat, it inflames without explosion, and burns with a yellow flame, with a residue of charcoal. Its solution has a bright yellow colour, reddens litmus paper, is extremely bitter, and acts like a strong acid on metallic oxides. It is said to be poisonous. (Journal of Science, ii. 210, and iii. 490.)

The salts of carbazotic acid are for the most part crystallizable, of a yellow colour, and brilliant lustre. They have the property, when rapidly heated, either of detonating like fulminating silver, or of burning rapidly with scintillations. The sparing solubility of carbazotate of potassa is the cause of carbazotic acid being used as a test of that alkali.

According to the analysis of Liebig, carbazotic acid contains no hydrogen, and its ingredients are expressed by the formula $C^{15}N^{3}O^{15}$, its equivalent being 254.25, or the sum of the equivalents of its elements. Buff and Dumas give different proportions, and the latter found 1.4 per cent. of hydrogen. It is certain, however, that it is a highly oxidized body, which accounts for the detonating property of its salts. Dumas and Liebig concur in representing the ratio of oxygen and nitrogen to be the same as in nitric acid.

Carbazotic acid is generated by the action of nitric acid on many substances both animal and vegetable, especially on those which contain nitrogen. The bitter principle, formed with nitric acid and silk by Welter, and by Braconnot from aloes, is carbazotic acid. It is also formed by digesting indigotic acid in nitric acid, with formation of binoxide of nitrogen, carbonic and oxalic acid, and, according to Dumas, of ammonia.

The substances called resin and artificial tannin, formed during the preceding process, consist of a brown friable matter united or mixed with different proportions of indigotic and nitric acid. It is insoluble in water and alcohol; but it is dissolved by the pure alkalies and their carbonates, and is precipitated from the solution by acids. It is best procured by boiling 1 part of indigo with 2 of nitric acid diluted with 15 or 20 of water, being purified by hot water from indigotic acid. In order to separate it from unchanged indigo, it is dissolved by carbonate of potassa, and precipitated by an acid.

SECTION II.

VEGETABLE ALKALIES.

Under this title are comprehended those proximate vegetable principles which are possessed of alkaline properties. The honour of discovering the existence of this class of bodies is due to Sertuerner, a German apothecary, who published an account of morphia so long ago as the year 1803; but the subject excited no notice until the publication of his second essay in 1816. The chemists who have since cultivated this department with most success are M. Robiquet, and MM. Pelletier and Caventou.

All the vegetable alkalies which have been analyzed consist of carbon, hydrogen, nitrogen, and oxygen; and it is remarked, which shows a close analogy of composition, that a single equivalent of each alkali contains exactly one equivalent of nitrogen. They are decomposed with facility by nitric acid and by heat, and ammonia is always one of the products of the destructive distillation. They never exist in an insulated state in the plants which contain them; but are apparently in every case combined with an acid, with which they form a salt more or less soluble in water. These alkalies are for the most part very insoluble in water, and of sparing solubility in cold alcohol; but they are all readily dissolved by that fluid at a boiling temperature, being deposited from the solution, commonly in the form of crystals, on cooling. Most of the salts are far more soluble in water than the alkalies themselves, and several of them are remarkable for their solubility.

Serullas observed that iodic acid is disposed to form with most of the vegetable alkalies supersalts, which are very insoluble in alcohol, and he proposed this property as a test of vegetable alkalies. It suffices to dissolve a vegetable alkali, especially quinia or cinchonia, or any of their salts, in alcohol, and to add, drop by drop a solution of iodic acid, so that it may be in excess: a supersalt is generated, which, though in very minute quantity, is immediately precipitated. The iodic acid, being itself insoluble in alcohol, should be so far diluted with water until it ceases to give a precipitate with strong alcohol. The aqueous solution of chloride of iodine, which contains iodic acid, may be substituted for the pure acid. (An. de Ch. et de Ph. xlv. 68.) It should be remembered in employing this test, that all the iodates are of sparing solubility;—that a little potassa, dissolved in alcohol, would give a precipitate on the addition of iodic acid. Care should be taken also in drying the iodate of a vegetable alkali, since when sharply heated they detonate powerfully.

As the vegetable alkalies agree in several of their leading chemical properties, the mode of preparing one of them admits of being applied with slight variation to all. The general outline of the method is as follows:—The substance containing the alkaline principle is digested, or more commonly macerated, in a large quantity of water, which dissolves the salt, the base of which is the vegetable alkali. On adding some more powerful salifiable base, such as potassa or ammonia, or boiling the solution for a few minutes with lime or pure magnesia, the vegetable alkali is separated from its acid, and being in that state insoluble in water, may be collected on a filter and washed. As thus procured, however, it is impure, retaining some of the other principles, such as the oleaginous, resinous, or colouring matters with which it is associated in the plant. To purify it from these substances, it should be mixed with a little animal charcoal, and dissolved in boiling alcohol. The alcoholic solution, which is to be filtered while hot, yields the pure alkali, either on cooling or by evaporation; and if not quite colourless, it should again be subjected to the action of alcohol and animal charcoal. In order to avoid the necessity of employing a large quantity of alcohol, the following modification of the process may be adopted. The vegetable alkali, after being precipitated and collected on a filter, is made to unite with some acid, such as the acetic, sulphuric, or hydrochloric, and the solution boiled with animal charcoal, until the colouring matter is removed. The alkali is then precipitated by ammonia or some other salifiable base.

The following table, formed principally from analyses by Liebig (An. de Ch. et de Ph. xlvii. 199), represents the composition of the vegetable alkalies in their anhydrous state. The numeral attached to each symbol indicates the number of equivalents of that element in one equivalent of the alkali. The elements of those whose atomic constitution is unknown, are given in relation to 100 parts.

ALKALIES.	Carb.	Hyd.	Nitrog.	Oxy.	Equiv.	Formulæ.
Morphia . .	208.08	+18	+14.15	+48	= 288.23	$C^{34}H^{18}N^{1}O^{6}$
Narcotina .	65	+ 5.5	+ 2.51	+26.99	in 100 parts.	
Codeia . .	189.72	+20	+14.15	+40	= 263.87	$C^{31}H^{20}N^{1}O^{5}$
Narceia . .	54.73	+ 6.52	+ 4.33	+34.42	in 100 parts.	
Cinchonia .	122.4	+12	+14.15	+ 8	= 156.55	$C^{20}H^{12}N^{1}O^{1}$
Quinia . .	122.4	+12	+14.15	+16	= 164.55	$C^{20}H^{12}N^{1}O^{2}$
Aricina . .	122.4	+12	+14.15	+24	= 172.55	$C^{20}H^{12}N^{1}O^{3}$
Strychnia .	183.6	+16	+14.15	+24	= 237.75	$C^{30}H^{16}N^{1}O^{3}$
Brucia . .	195.84	+18	+14.15	+48	= 275.99	$C^{32}H^{18}N^{1}O^{6}$
Veratria . .	208.08	+22	+14.15	+48	= 292.23	$C^{34}H^{22}N^{1}O^{6}$
Emetia . .	64.57	+ 7.77	+ 4.3	+22.95	in 100 parts.	
Delphia . .	76.69	+ 8.89	+ 5.93	+ 7.49	in 100 parts.	

Morphia.

This alkali is the medicinal agent of opium, in which it exists combined with meconic and sulphuric acid, and associated with several other substances, especially with narcotina, codeia, narceia, meconin, gummy, resinous, and extractive colouring matters, lignin, fixed oil, and a small quantity of caoutchouc. The first step in its preparation consists in cutting a given quantity of opium into small pieces, pouring on it distilled water, and macerating for two or three days at a temperature not exceeding 100°, aided by frequent agitation; the first infusion is then decanted, and a second and a third conducted in a similar manner, so that the soluble parts should be completely extracted. A highly coloured but clear solution is thus obtained, which has the peculiar odour of opium, is distinctly acid to test paper, and contains all the meconate and sulphate of morphia, together with the associated alkalies, contained in the specimen. To obtain pure morphia from the solution one of two modes is now commonly employed. The first consists in concentrating the aqueous solution of opium, and adding a slight excess of ammonia, when the morphia and narcotina are precipitated. The precipitate is digested at 120° or 130° in proof spirit, which takes up most of the narcotina and colouring matter: the morphia is then dissolved in strong boiling alcohol, from which it is deposited by cooling and evaporation. The object of the second is to obtain the morphia in the form of a hydrochlorate, by which means its separation from narcotina is more fully accomplished than by the former method; and the following process, devised by Drs. Gregory and Robertson, of Edinburgh, may be safely employed. (Edin. Med. and Surg. Journal, Nos. 107 and 111.) The aqueous solution of opium is concentrated in a vessel of tinned iron, or other evaporator, to the consistence of a thin syrup, when a slight excess of chloride of calcium, neutral and quite free from iron, is added; the mixture is boiled for a few minutes, and then poured into an evaporating basin. When cold, the hydrochlorates are taken up in water, which is added until a copious separation of resinous flocks ensues, leaving the insoluble meconate and sulphate of lime with a good deal of colouring matter. The clear liquid is again evaporated to a syrupy consistence, a little marble being added to ensure perfect neutrality, the warm fluid is poured off the sediment into a clean capsule, and is well stirred during crystallization. The mass is then put into a stout cloth, and the liquid part, containing chloride of calcium, the hydrochlorate of narcotina, and colouring matter, is pressed out from the crystallized hydrochlorate of morphia: this impure salt is redissolved in water at 70°, filtered through cloth, mixed with a little fresh chloride of calcium, crystallized, and compressed as before. It is taken up in hot water, digested for about 24 hours with animal charcoal, filtered, evaporated, crystallized, and squeezed in cloth as on former occasions; but in this part of the process a little free hydrochloric acid may be added with advantage, as it holds in solution any remaining colouring matter, and renders the crystallization of the hydrochlorate of morphia more perfect. The pure salt is then dried at a temperature of 150°, and amounts on an average to 10 per cent. of the opium used, corresponding to 9.43 per cent. of crystallized morphia. It contains a small quantity of hydrochlorate of codeia, which is left in solution when the morphia is precipitated by ammonia. The absence of narcotina may be proved by the following character:—If dissolved in distilled water, and pure potassa be added, crystals of morphia at first subside, which are completely redissolved by an excess of the potassa; but when narcotina is present, the alkali occasions a peculiar milkiness, and by heat woolly flocks are separated.

Pure morphia crystallizes readily when its alcoholic solution is evaporated, and yields colourless crystals of a brilliant lustre. They mostly occur in irregular six-sided prisms with dihedral summits; but their primary form is a right rhombic prism, of which the lateral planes only appear in the crystals (Brooke). According to Liebig, they consist of 288.23 parts, or one eq. of anhydrous morphia, and 18 or two eq. of water, which they give out at 248°, the loss amounting to 6.33 per cent. (An. de Ch. et de Ph. xlvii. 198). Morphia is almost wholly insoluble in cold, and to very small extent in hot water. It is soluble in strong alcohol especially by the aid of heat. In its pure state it has scarcely any taste; but when rendered soluble by combining with an acid or by solution in alcohol, it is intensely bitter. It has an alkaline reaction, and combines with acids, forming neutral salts, which are far more soluble in water than morphia itself, and for the most part are capable of crystallizing. Solutions of pure potassa and soda dissolve it, as in some measure does ammonia.

Strong nitric acid decomposes morphia, forming a red solution, which by the continued action of the acid acquires a yellow colour, and is ultimately converted into oxalic acid. Nitric acid has a similar effect on brucia. With a persalt of iron morphia strikes a blue tint.

Morphia is the narcotic principle of opium. When pure, owing to its insolubility, it is almost inert; for Orfila gave twelve grains of it to a dog without its being followed by any sensible effect. In a state of solution, on the contrary, it acts on the animal system with great energy, Sertuerner having noticed alarming symptoms from so small a quantity as half a grain. From this it appears to follow that the effects of an over-dose of a salt of morphia may be prevented or diminished by giving a dilute solution of ammonia, or an alkaline carbonate, so as to precipitate the vegetable alkali.

When opium is administered as a poison, its presence is rendered obvious by the peculiar odour of that drug, as well as by the red tint given to persalts of iron by the meconic acid of the opium; but when death is occasioned by a salt of morphia, it becomes necessary to eliminate the *morphia*, a practical process of considerable delicacy. The method *suggested by* Lassaigne for detecting acetate of morphia, may be applied to its saline combinations in general (An. de Ch. et de Ph. xxv. 102.) The suspected solution is evaporated by a temperature of 212°, and the residue treated with alcohol, by which the salt of morphia, together with osmazome and some salts, is dissolved. The alcohol is next evaporated, and water added to separate fatty matter. The aqueous solution is then set aside for spontaneous evaporation, during which the salt of morphia is generally deposited in crystals. From an aqueous solution of the salt, ammonia throws down a crystalline precipitate, which may be recognized as morphia by the combination of the following characters:—By the figure of its crystals; its bitter taste; solubility in alcohol; alkalinity; by the orange-red tint developed by nitric acid; and by the peculiar action of iodic acid. The last character is particularly valuable in distinguishing morphia from other vegetable alkalies: the latter combine with iodic acid and form iodates; but morphia decomposes iodic acid, and sets iodine free, which may then be detected by starch. A grain of morphia in 7000 grains of water may be discovered by this test. (Serullas.)

Salts of Morphia.—These are best prepared by dissolving pure morphia in dilute acid, and evaporating the solution. The neutral sulphate crystallizes in bunches of acicular crystals, which consist of one equivalent of morphia, one equivalent of acid, and six equivalents of water: on drying at 248°, four equivalents of water are expelled; but the rest of the water cannot be driven off without decomposing the salt itself, and, therefore, seems essential to its constitution. The water lost by heat is absorbed from the atmosphere as the sulphate cools. Morphia also forms a bisulphate.

Hydrochlorate of morphia may be generated by the direct action of hydrochlorate acid gas on anhydrous morphia (Liebig), by dissolving the alkali in dilute hydrochloric acid, or by the process of Gregory, above described. It commonly crystallizes in turfs of acicular crystals, which are neutral, are anhydrous, and contain an equivalent of acid and of base.

Acetate of morphia, though till lately much employed in medical practice, is less convenient for that purpose than the hydrochlorate, being variable in constitution. To procure it in the solid state, it must be evaporated to dryness, and in this process some of its acid is usually expelled. It is deliquescent, and is hence with difficulty preserved in a constant state of dryness; and when neutral it is decomposed by water, whereby part of the morphia is rendered insoluble. In fact, the best mode of employing the acetate is to dissolve given weights of morphia in dilute acetic acid, and preserve it in that form, taking care that the acid is in excess. The basis of Battley's sedative liquor is supposed to be acetate of morphia.

Narcotina.—This substance was described in 1803 by Derosne, and was long called *the salt of Derosne;* Sertuerner supposed it to be meconate of morphia; but Robiquet proved that it is an independent principle, and applied to it the name of *narcotine.* It is easily prepared by digesting the aqueous extract of opium, or the precipitate by ammonia from the aqueous infusion, in sulphuric ether, in which meconate of morphia and morphia are insoluble, but which take up all the narcotina and deposites it in regular crystals by evaporation. It may be further purified by animal charcoal and a second crystallization. A convenient mode of separating it from morphia without sulphuric ether, suggested by Dr. Robertson in the essay above cited, is to boil the impure morphia in water, and add successive portions of sal ammoniac as long as ammonia escapes: the morphia at a boiling temperature decomposes that salt, and the resulting hydrochlorate of morphia is of course dissolved; while all the narcotina is left in a pulverulent form. Other salts of morphia may be made in like manner by employing a corresponding salt of ammonia. This fact, of the decomposition of ammoniacal salts by morphia, is due to M. Buisson, who finds that most of the vegetable alkalies in general possess the same property at a high temperature.

Narcotina is insoluble in cold and very slightly soluble in hot water. It dissolves in oil, ether, and alcohol; the latter, though diluted, acting as a solvent for it by the aid of heat. It is not alkaline to test paper, but unites definitely with hydrochloric acid, forming a salt extremely soluble in water, which crystallizes in needles from an alcoholic solution. Robiquet also obtained the crystallized sulphate. Its presence in the aqueous infusion of opium is due to a free acid, and yet uncombined narcotina is dissolved from crude opium by sulphuric ether: it acts so feebly as a base, that it is separated from its acid either by the ether, or probably by the force of crystallization. A similar cause may account for the variable composition of its salts, the equivalent of narcotina having been estimated from the hydrochlorate at 319 by Pelletier, at 560 by Liebig, and at 408 by Robiquet (An. de Ch. et de Ph. li. 231).

Narcotina acts much less energetically on the animal economy than morphia. The stimulating action of opium is partly ascribed to narcotina; and the opinion is supported by the experience of medical practitioners, who find that pure morphia acts more agreeably and safely than when narcotina is present.

Codeia.

This alkali was discovered in 1832 by Robiquet in hydrochlorate of morphia, made by Gregory's process (An. de Ch. et de Ph. li. 259.) It appears that hydrochlorate of codeia crystallizes along with the salt of morphia, and is present in variable quantity: in hydrochlorate of morphia from East-India opium Christison obtained 1-12th of hydrochlorate of codeia, and Gregory 1-30th from the hydrochlorate prepared with Turkey opium. On dissolving the mixed hydrochlorates in water, and precipitating the morphia by ammonia, the codeia remains in solution, and crystallizes by subsequent evaporation. On dissolving in hot ether, it is obtained by spontaneous evaporation in acicular crystals or flat prisms, which, when pure, are quite colourless and transparent.

Codeia fuses at 300° without decomposition, and at a high temperature burns with flame without residue. Water at 60° dissolves 1.26 per cent., 3.7 at 110°, and 5.9 at 212°. When more of it is present than boiling water can dissolve, the excess fuses, and forms a stratum of an oily aspect at the bottom. The solution is distinctly alkaline, and yields neutral salts with alkalies, some of which, especially the nitrate, crystallize with facility. It is distinguished from morphia by the form and aspect of its crystals, greater solubility in water, solubility in boiling ether, insolubility in solutions of the pure alkalies, by yielding a copious precipitate with tincture of gall-nuts, and not being reddened by nitric acid. Its crystals consist of 263.87 parts or one eq. of codeia and 18 or two eq. of water, which is dissipated at 212°.

Narceia.

This alkali was discovered by Pelletier in 1832 (An. de Ch. et de Ph. l. 252), and is contained in the aqueous infusion of opium, probably in combination with meconic acid. After precipitating the morphia and narcotina by ammonia, meconic acid by pure baryta, and the excess of baryta by carbonate of ammonia, the solution is boiled to expel the latter salt, and then evaporated to the consistence of syrup. The residue, set at rest for some days in a cool place, yields crystals which, after compression in linen to remove adhering liquid, should be dissolved in boiling strong alcohol, and recrystallized by evaporation. The residue consists of narceia, together with some narcotina, meconin, and fatty matter: the three last are taken up by digestion in sulphuric ether, in which the narceia is insoluble. It is purified by crystallization from alcohol or water, to which a little animal charcoal is added.

Pure narceia is white, and crystallizes in needles or small prisms. It is inodorous, and has a faint bitter taste, with slight pungency. It fuses at 198°, becomes yellow at 220°, and at high temperatures is decomposed, yielding among other products a peculiar volatile acid. It is soluble in 375 times its weight of cold and 230 of boiling water, and dissolves freely in hot alcohol, but it is insoluble in ether. It is decomposed by the stronger acids, but unites with them when diluted, acting as a feeble alkali, which neutralizes acids imperfectly, though some of its salts are crystallizable. Its salts, with the stronger acids especially, have the peculiarity of being blue in a certain degree of concentration, and on adding successive quantities of water, the colour changes to violet and rose-red, and lastly disappears. By this character, added to its light fusibility, and the action of solvents, it is distinguished from the other principles with which it is associated in opium. Its equivalent has not been determined.

Cinchonia and Quinia.

The existence of a distinct vegetable principle in cinchona bark was inferred by the late Dr. Duncan in the year 1803, who ascribed to it the febrifuge virtues of the plant, and proposed for it the name of *cinchonin* (Nicholson's Journal, 1803). Dr. Gomez of Lisbon, whose attention was directed to the subject by the researches of Dr. Duncan, succeeded in procuring cinchonin in a separate state; but its alkaline nature was first discovered in 1820 by Pelletier and Caventou (An. de Ch. et de Ph. xv.) It has been fully established by the labours of those chemists that the febrifuge property of bark is possessed by two alkalies, the *cinchonia*, or cinchonin of Dr. Duncan, and *quinia*, both of which are combined with kinic acid. These principles, though very analogous, are distinctly different, standing in the same relation to each other as potassa and soda. Cinchonia exists in the *Cinchona condaminea*, or pale bark; quinia, often with a little cinchonia, is present in *C. cordifolia*, or yellow bark; and they are both contained in *C. oblongifolia*, or red bark. One of the easiest processes for preparing them, is to take up the soluble parts of the bark by hot water acidulated with hydrochloric acid, concentrate the solution, and then digest with successively added portions of slaked lime, until the liquid is distinctly alkaline. The precipitate is carefully collected, and the vegetable alkali separated from it by boiling alcohol. Slight modifications of the method have been proposed by Badollier and Voreton. From one pound of yellow bark, Voreton procured 80 grains of quinia, which is nearly 1.4 per cent. (An. de Ch. et de Ph. xvii); but the quantity obtained from different varieties of bark is very variable.

Cinchonia.—Pure cinchonia crystallizes in colourless quadrilateral prisms, which are anhydrous, require 2500 times their weight of boiling water for solution, and are insoluble in cold water. Its proper menstruum is boiling alcohol; but it is dissolved in small quantity by oils and ether. Its taste is bitter, though slow in being perceived, on account of its insolubility; but when the alkali is dissolved by alcohol or an acid, the bitterness is very powerful, and accompanied by the flavour of cinchona bark. Its alkaline properties are exceedingly well marked, since it neutralizes the strongest acids. The sulphate, hydrochlorate, nitrate, and acetate of cinchonia are soluble in water, and the sulphate crystallizes in very short six-sided prisms derived from an oblique rhomboidal prism. It commonly occurs in twin crystals; and is composed of 156.55 parts or one eq. of cinchonia, 40.1 parts or one eq. of sulphuric acid, and 36 parts or four eq. of water. It effloresces in a dry air, and gives out all its water when moderately heated. Cinchonia forms a disulphate, which is much less soluble than the neutral sulphate. The hydrochlorate is composed of single equivalents of base and acid, fuses at 212°, is readily soluble in water and alcohol, and crystallizes in shining acicular crystals. The neutral tartrate, oxalate, and gallate of cinchonia are insoluble in cold, but soluble in hot water, as well as in alcohol.

Quinia or Quinine.—This alkali is precipitated from its solution by alkalies in white flocks, which do not assume a crystalline appearance like cinchonia; and it crystallizes imperfectly even from an alcoholic solution. It is very soluble in alcohol, forming a solution which is intensely bitter, and possesses a distinct alkaline reaction. Ether likewise dissolves it, but it is almost insoluble in water. Its febrifuge virtues are more powerful than those of cinchonia, and it is now extensively employed in the practice of medicine.

The most important of the salts of quinia is the disulphate, which is made in large quantity for medical purposes. This compound crystallizes in delicate white needles, having the appearance of amianthus, has a very bitter taste, and is less soluble in water than sulphate of cinchonia. It is freely dissolved by boiling alcohol, and is neutral to test paper. It is composed of 329.1 parts or two eq. of quinia, 40.1 or one eq. of sulphuric acid, and 90 or ten eq. of water: when dried at 248°, it abandons eight equivalents of water, and retains the remainder until the salt itself is decomposed.

The sulphate of neutral composition is acid to test paper, and crystallizes in transparent square prisms, which effloresce in a dry air, and contain 24.66 per cent. of water, corresponding nearly to six eq. of water. This salt is much more soluble than the disulphate. The neutral gallate, tartrate, and oxalate of quinia, like the analogous salts of cinchonia, are insoluble in cold water.

From the new facts which have been ascertained relative to the constituents of bark, the action of chemical tests on a decoction of this substance is now explicable. According to the analysis of Pelletier and Caventou, the different kinds of Peruvian bark, besides the kinate of cinchonia or quinia, contain the following substances:—a greenish fatty matter; a red insoluble matter; a red soluble principle, which is a variety of tannic acid; a yellow colouring matter; kinate of lime; gum, starch, and lignin. It is hence apparent that a decoction of bark, owing to the tannic acid which it contains, may precipitate a solution of tartar emetic, of gelatin, or a salt of iron, without containing a trace of vegetable alkali, and consequently without possessing any febrifuge virtues. An infusion of gall-nuts, on the contrary, causes a precipitate only by its gallic acid uniting with cinchonia or quinia, and, therefore, affords a test for distinguishing a good from an inert variety of bark.

Sulphate of quinia, from its commercial value, is frequently adulterated. The substances commonly employed for the purpose are water, sugar, gum, starch, ammoniacal salts, and earthy salts, such as sulphate of lime and magnesia, or acetate of lime. Pure sulphate of quinia, when deprived of its water of crystallization by a heat of 212°, should lose only from 8 to 10 per cent. of water. Sugar may be detected by dissolving the suspected salt in water, and adding precisely so much carbonate of potassa as will precipitate the quinia. The taste of the sugar, no longer obscured by the intense bitter of the quinia, will generally be perceived; and it may be separated from the sulphate of potassa, by evaporating gently to dryness, and dissolving the sugar by boiling alcohol. Gum and starch are left when the impure sulphate of quinia is digested in strong alcohol. Ammoniacal salts are discovered by the strong odour of ammonia, which may be observed when the sulphate is put into a warm solution of potassa. Earthy salts may be detected by burning a portion of the sulphate. Several of the preceding directions are taken from a paper on the subject by Mr. Phillips. (Phil. Mag. and Ann. iii. 111.)

Aricina.—This alkali was observed by Pelletier and Corriol in 1829 in a sample of cinchona bark which had been substituted for the ordinary kinds of bark, and is very analogous to cinchonia and quinia in its properties. By reference to the table at page 524, it will be seen that these three alkalies have such an analogy of composition, that they may be viewed as oxides of the same compound radical, the formula of which is $C^{20}H^{12}N^{1}$. (An. de Ch. et de Ph. li. 186.)

Strychnia and Brucia.

Strychnia.—Strychnia was discovered in 1818 by Pelletier and Caventou in the fruit of the *Strychnos ignatia* and *Strychnos nux vomica*, and has since been extracted by the same chemists from the Upas. (An. de Ch. et de Ph. x. and xxvi.)

The most economical process for preparing this alkali is that recommended by M. Corriol. (Journal de Pharmacie for October 1825, p. 492.) It consists in treating *nux vomica* with successive portions of cold water, evaporating the solution to the consistence of syrup, and precipitating the gum by alcohol. The alcoholic solution is then evaporated to the consistence of an extract by the heat of a water-bath. The extract, which consists almost entirely of igasurate of strychnia, is dissolved by cold water, and by this means deprived of a little fatty matter, which had originally been dissolved, probably through the medium of the gum. The solution is next heated, and the strychnia precipitated by a slight excess of lime-water, and then dissolved by boiling alcohol. On evaporating the spirit, the alkali is obtained pure except in containing a little brucia and colouring matter, both of which are effectually removed by maceration in dilute alcohol.

Strychnia is very soluble in boiling alcohol, and is procured in minute four-sided prisms by allowing the solution to evaporate spontaneously. In this state it is anhydrous. It is almost insoluble in water, requiring more than 6000 parts of cold and 2500 of boiling water for solution; but notwithstanding its sparing solubility, it excites an insupportable bitterness in the mouth.—Water containing only 1-600,000th of its weight of strychnia has a bitter taste. It has a distinct alkaline reaction, and neutralizes acids, forming salts, most of which are soluble in water. It is united in the *nux vomica* and St. Ignatius's bean with igasuric acid (page 520). By the action of strong nitric acid it yields a red colour; but it appears from some observations of Pelletier and Caventou, that the red tint is owing to the presence of some impurity, which is probably brucia.

Strychnia is one of the most virulent poisons hitherto discovered, and is the poisonous principle of the substance in which it is contained. Its energy is so great, that half a grain blown into the throat of a rabbit occasioned death in the course of five minutes. Its operation is always accompanied with symptoms of locked jaw and other tetanic affections.

Hydrochlorate of strychnia is a soluble neutral salt, which crystallizes readily in tufts of minute quadrilateral prisms or needles. It consists of 237.75 parts or one eq. of base and 36.42 or one eq. of acid. The neutral sulphate crystallizes in small transparent cubes, which consist of single equivalents of base and acid, united with three eq. of water. The salt when heated fuses in its water of crystallization, and is rendered anhydrous. It requires ten times its weight of water for solution.

Brucia.—This alkali was discovered in the *Brucea antidysenterica* by Pelletier and Caventou, soon after their discovery of strychnia (An. de Ch. et de Ph. xii.); and it likewise exists in small quantity in the St. Ignatius's bean and *nux vomica*. In its bitter taste and poisonous qualities, it is very similar to strychnia, but is twelve or sixteen times less energetic. It is soluble both in hot and cold alcohol, especially in the former; and it crystallizes when its solution is evaporated. Its crystals dried at 240° lose about 19 per cent. of water, and are hence composed of 275.99 parts or one eq. of the acid to 72 parts or eight eq. of water. Even dilute alcohol by aid of heat dissolves brucia, and on this property is founded the method of separating it from strychnia. It is more soluble in water than most of the other vegetable alkalies, requiring only 850 times its weight of cold, and 500 of boiling water for solution. With nitric acid it acquires a deep blood-red colour, which afterwards passes into yellow; and when either of these changes has taken place, the addition of protochloride of tin produces a pretty violet tint, and a precipitate of the same colour subsides.

Veratria, Emetia, Picrotoxia, Corydalia, Solania, &c.

Veratria.—The medicinal properties of the seeds of the *Veratrum sabadilla*, and of the root of the *Veratrum album*, or white hellebore, and *Colchium autumnale* or meadow saffron, are owing to the peculiar alkaline principle *veratria*, which was discovered by Pelletier and Caventou in 1819 (Journ. de Pharm. vi.). To a decoction of the bruised seeds of the Veratrum sabadilla add acetate of oxide of lead as long as a precipitate falls, by which means extractive matter is thrown down: the filtered solution is deprived of lead by hydrosulphuric acid, the excess of the gas expelled by heat, and the solution boiled with magnesia or slaked lime until it is rendered alkaline. The precipitate collected, dried, and boiled in alcohol, yields a solution of veratria, which may be decolorized by digestion with animal charcoal, and be obtained by evaporation. It may be procured from the roots of the two other plants by a similar process. This alkali, which appears to exist in those plants in combination with gallic acid, is white and pulverulent, has not been obtained in crystals, fuses at 280°, is inodorous, and of an acrid taste. It requires 1000 times its weight of boiling, and still more of cold water for solution. It is very soluble in alcohol, and may also be dissolved, though less readily, by means of ether. It has an alkaline reaction, and neutralizes acids; but it is a weaker base than morphia, quinia, or strychnia. It acts with singular energy on the membrane of the nose, exciting violent sneezings though in very minute quantity. When taken internally in very small doses, it produces excessive irritation of the mucous coat of the stomach and intestines; and a few grains were found to be fatal to the lower animals.

M. Couerbe has prepared the sulphate and hydrochlorate in crystals, and determined the probable equivalent of veratria as given at page 524. (An. de Ch. et de Ph. lii. 376.)

Emetia.—Ipecacuanha consists of an oily matter, gum, starch, lignin, and a peculiar principle, which was discovered in 1817 by Pelletier, and to which he has applied the name of *emetine*. (Journal de Pharmacie, iii.) In order to extract this alkali, the oily matter is first removed by digesting the powdered root in ether, and the emetia is next taken up by boiling alcohol, which is diluted with water, and the spirit expelled by distillation. Some more fatty matter is thus separated: the emetia is then thrown down by boiling the aqueous solution with magnesia. It may be decolorized by animal charcoal in the usual manner. Emetia, of which ipecacuanha contains 16 per cent., appears to be the sole cause of the emetic properties of that root.

Emetia is a white pulverulent substance, of a rather bitter and disagreeable taste, sparingly soluble in cold, but more freely in hot water, and insoluble in ether. It is readily dissolved by alcohol. At 122° it fuses. It has a distinct alkaline reaction, and neutralizes acids; but its salts are little disposed to crystallize. (An. de Ch. et de Ph. xxiv. 181.)

Picrotoxia.—The bitter poisonous principle of *Cocculus indicus* was discovered in 1819 by M. Boullay, who gave it the name of *picrotoxine.* Its claim to the title of a vegetable alkali, among which class of bodies it was placed by its discoverer, has been called in question by M. Cassaseca, from whose remarks it seems that picrotoxia has no alkaline reaction, and does not neutralize acidity. It combines, however, with acids, and with the acetic and nitric acids forms crystallizable compounds. According to Oppermann 100 parts of picrotoxia contain of carbon 61.434, hydrogen 6.11, and oxygen 32.456. It appears, also, that the menispermic acid, supposed by M. Boullay to be united in *Cocculus indicus* with picrotoxia, is merely a mixture of sulphuric and malic acids. (Edinburgh Journal of Science, v.)

Corydalia.—This alkali, discovered by Dr. Wackenroder, is contained in the root of the fumitory, (not the common fumitory, *Fumaria officinalis*, but) *Fumaria cava* and *Corydalis tuberosa* of Decandolle. It exists in the plant as a soluble malate, is precipitated from its aqueous solution by magnesia, and is purified by alcohol.

It is soluble in alcohol, and the hot saturated solution in cooling yields colourless prismatic crystals of a line in length. By spontaneous evaporation fine laminæ are formed. It is likewise soluble in ether, but very sparingly in water. It is insipid and inodorous; but when dissolved by acids or alcohol it is very bitter. Its solution has an alkaline reaction, and it neutralizes acids. Cold dilute nitric acid dissolves it and yields a colourless solution; but when heated it acquires a red tint, and becomes blood-red when concentrated. Its salts are precipitated by potassa, pure or carbonated, and by infusion of gall-nuts. The precipitate is white when the solution is dilute, and grayish-yellow if concentrated. (Phil. Mag. and An. iv. 153.)

Solania.—The active principle of the *Solanum dulcamara*, or woody nightshade, was procured in a pure state by Desfosses; and the same alkali exists in other species of *solanum.* Solania is combined in the plant with malic acid, and is thrown down of a gray colour by ammonia from the expressed and filtered juice of the ripe berries. After being well washed and dried, it is purified by solution in hot alcohol, from which by slow evaporation it is deposited as a white powder with a pearly lustre. It is insoluble in cold water, and requires 8000 times its weight of hot water for solution. Alcohol is its proper menstruum: it is sparingly dissolved by ether, and is insoluble in oil. It has a distinct alkaline reaction, and with acids forms neutral salts, which have a bitter taste. (Journ. de Pharm. vi. and vii.)

Cynopia.—Professor Ficinus of Dresden has discovered a new alkali in the *Æthusa Cynapium*, or lesser hemlock, to which he has given the name of *Cynopia.* It is crystallizable, and soluble in water and alcohol, but not in ether. The crystals are in the form of a rhombic prism, which is also that of the crystals of the sulphate.

Delphia.—This substance was discovered about the same time by Feneuille and Lassaigne in France, and Brandes in Germany, in the seeds of the *Delphinium Staphysagria* or *Stavesacre.* It is easily prepared by digesting the seeds in water acidulated with sulphuric acid, and precipitating by magnesia or other alkaline substance. It is then purified in the usual manner by solution in alcohol and digestion with animal charcoal. It is left by evaporation as a white crystalline powder, which is almost insoluble in water, but is dissolved by alcohol, ether, and the oils. It has a feeble alkaline reaction, and yields neutral salts of a bitter taste, but which rarely crystallize. (An. de Ch. et de Ph. xii. and lii. 364.)

Althea was announced by M. Bacon of Caen as a new vegetable alkali, said to be procured from the root of the marsh-mallow (Althæa Officinalis). According to M. Plisson this alkali has no existence, and what was thought to be supermalate of althea is asparagin. From the experiments of Wittstock it appears that the asparagin found by Plisson does not exist in the plant itself: the aqueous solution of the marsh-mallow contains sugar, a mucilaginous matter, and a peculiar vegetable acid containing nitrogen, which is united with magnesia; and by the mutual action of these ingredients of the solution, the asparagin or althein is generated. (Pog. Annalen, xx. 346.)

Sanguinaria is a vegetable alkali, obtained by M. Dana from the *Sanguinaria Canadensis*, called *blood-root* in America, from the red colour of its juice. The powdered root is digested in pure alcohol, and the red solution mixed with a little ammonia is poured into water, when a brown matter subsides. After washing carefully, and removing colouring matter by animal charcoal, the alkali is removed by hot alcohol, and obtained by evaporation as a pearly white matter of an acrid taste and alkaline reaction. By exposure to air it becomes yellow. It is insoluble in water, but is dissolved by alcohol and ether. Its salts have a red colour. (Phil. Mag. and An. v. 151.)

Nicotina.—This alkali was extracted by MM. Posselt and Reimann from the leaves of tobacco, and also exists in the seeds. At common temperatures, and even at 21°, it is a liquid, usually of a yellow tint, but colourless and transparent when pure; it has a pungent odour like that of tobacco, and an acrid burning taste which lasts a long time. It is highly poisonous, a single drop being fatal to a dog. It rises in vapour at 212°, and boils at 475°, but is decomposed at the same time. Water dissolves it in all proportions, and it is very soluble in ether, which withdraws it from its aqueous solution. It has a distinct alkaline reaction, and forms with acids neutral salts, several of which are crystallizable.

Besides the vegetable alkalies, already described, it has been rendered highly probable, chiefly by the researches of M. Brandes, that several other plants, such as the *Atropa belladonna*, *Conium maculatum*, *Hyoscyamus niger*, *Datura stramonium*, and *Digitalis*, owe their activity to the presence of an alkali. Vauquelin rendered it probable that an alkali is contained in the *Daphne mezereum*, to which, if it exist, the name of daphnia may be applied.

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SECTION III.

NEUTRAL SUBSTANCES, THE OXYGEN AND HYDROGEN OF WHICH ARE IN THE SAME RATIO AS IN WATER.

The substances contained in this section are remarkable for a close resemblance in the ratio of their elements. They may be viewed, like several of the vegetable acids (page 497), as hydrates of carbon; though in all probability their elements are combined with each other in a very different order. The proportions in which they unite with other bodies is so imperfectly known, that their atomic constitution has not been satisfactorily determined. Their composition, stated in 100 parts, is as follows:—

	Carbon.	Hydrogen.	Oxygen.	Analyzed by
Pure cane sugar	42.85	6.35	50.8	Prout.
Mannite .	38.7	6.8	54.5	Do.
Wheat starch	43.55	6.77	49.68	Gay-Lussac and Thenard.
Potato starch	44.25	6.67	49.08	Berzelius.
Gum-arabic	42.23	6.93	50.84	Gay-Lussac and Thenard.
Lignin .	51.45	5.82	42.73	Gay-Lussac and Thenard.

Sugar.

Sugar is an abundant vegetable product, existing in a great many ripe fruits, though few of them contain it in sufficient quantity for being collected. The juice which flows from incisions made in the trunk of the American maple tree, is so powerfully saccharine that it may be applied to useful purposes. Sugar was prepared in France and Germany during the late war from the beet-root; and this manufacture is at present carried on in France on a scale of considerable magnitude. Proust extracted it in Spain from grapes. But most of the sugar at present used in Europe is obtained from the sugar-cane (*Arundo saccharifera*), which contains it in a greater quantity than any other plant. The process, as practised in our West India Islands, consists in evaporating the juice of the ripe cane by a moderate and cautious ebullition, until it has attained a proper degree of consistence for crystallizing. During this operation lime-water is added, partly for the purpose of neutralizing free acid, and partly to facilitate the separation of extractive and other vegetable matters, which unite with the lime and rise as a scum to the surface. When the syrup is sufficiently concentrated, it is drawn off into shallow wooden coolers, where it becomes a soft solid composed of loose crystalline grains. It is then put into barrels with holes in the bottom, through which a black ropy juice, called molasses or treacle, gradually drops, leaving the crystallized sugar comparatively white and dry. In this state it constitutes raw or muscovado sugar.

Raw sugar is further purified by boiling a solution of it with white of eggs, or the serum of bullock's blood, lime-water being generally employed at the same time. When properly concentrated, the clarified juice is received in conical earthen vessels, the apex of which is undermost, in order that the fluid parts may collect there, and be afterwards drawn off by the removal of a plug. In this state it is loaf or refined sugar. In the process of refining sugar, it is important to concentrate the syrup at a low temperature; and on this account a very great improvement was introduced some years ago by conducting the evaporation *in vacuo*.

Pure sugar is solid, white, inodorous, and of a very agreeable taste. It is hard and brittle, and when two pieces are rubbed against each other in the dark, phosphorescence is observed. It crystallizes in the form of four or six-sided prisms bevelled at the extremities. The crystals are best made by fixing threads in syrup, which is allowed to evaporate spontaneously in a warm room; and the crystallization is promoted by adding spirit of wine. In this state it is known by the name of *sugar-candy*.

Sugar undergoes no change on exposure to the air; for the deliquescent property of raw sugar is owing to impurities. It is soluble in an equal weight of cold, and to almost any extent in hot water. It is soluble in about four times its weight of boiling alcohol, and the saturated solution, by cooling and spontaneous evaporation, deposites large crystals. When the aqueous solution of sugar is mixed with yeast, it undergoes the vinous fermentation, the theory of which will be explained in a subsequent section.

Sugar unites with the alkalies and alkaline earths, forming compounds in which the taste of the sugar is greatly injured; but it may be obtained again unchanged by neutralizing with sulphuric acid, and dissolving the sugar in alcohol. When boiled with oxide of lead, it forms an insoluble compound, which consists of 58.26 parts of oxide of lead, and 41.74 parts of sugar (Berzelius); but it is not precipitated by acetate or subacetate of oxide of lead.

Sulphuric acid decomposes sugar with deposition of charcoal; and nitric acid causes the production of oxalic acid, as already described in a former section. The vegetable acids diminish the tendency of sugar to crystallize.

Sugar is very easily affected by heat, acquiring a dark colour and burned flavour. At a high temperature it yields the usual products of the destructive distillation of vegetable matter, together with a considerable quantity of pyromucic acid.

Sugar as obtained from different sources varies somewhat in composition. The largest quantity of carbon was found by Prout in cane sugar as exemplified in sugar-candy and the best loaf-sugar, dried at 212°, which contain 42.85 per cent.; while sugar from honey contains only 36.36 per cent. of carbon. He considers the sugar from starch, diabetic urine, and grapes, to be nearly the same as that from honey. The sugar from the maple-tree and the beet-root corresponds with cane sugar; but the quantity of carbon in these varieties appears to vary from 40 to 42.85 per cent. (Phil. Trans. 1827.) If sugar with 40 per cent. of carbon be taken as standard sugar, we may consider sugar as containing carbon, hydrogen, and oxygen in the ratio of their equivalents.

Molasses.—The saccharine principle of treacle has been supposed to be different from crystallizable sugar; but it chiefly consists of common sugar, which is prevented from crystallizing by the presence of foreign substances, such as saline, acid, and other vegetable matters.

Sugar of Grapes.—The sugar procured from the grape has the essential properties of cane sugar, though not quite so sweet; and it contains rather less carbon. The saccharine principle of the acidulous fruits has not been particularly examined. It is obtained with difficulty in a pure state, owing to the presence of vegetable acids, which prevent it from crystallizing.

A saccharine substance similar to that from grapes may be procured from several vegetable principles, such as starch and the ligneous fibre, by the action of sulphuric acid.

Honey.—According to Proust, honey consists of two kinds of saccharine matter, one of which crystallizes readily and is analogous to common sugar, while the other is uncrystallizable. They may be separated by mixing honey with alcohol, and pressing the solution through a piece of linen. The liquid sugar is removed, and the crystallizable portion is left in a solid state. Besides sugar it contains mucilaginous, colouring, and odoriferous matter, and probably a vegetable acid. Diluted with water, honey is susceptible of the vinous fermentation without the addition of yeast.

The natural history of honey is as yet imperfect. It is uncertain whether honey is merely collected by the bee from the nectaries of flowers, and then deposited in the hive unchanged, or whether the saccharine matter of the flower does not undergo some change in the body of the animal.

Manna.—This saccharine matter is the concrete juice of several species of ash, and is procured in particular from the *Fraxinus ornus*. The sweetness of manna is owing, not to sugar, but to a distinct principle, called *mannite*, which is mixed with a peculiar vegetable extractive matter. Manna is soluble both in water and boiling alcohol, and the latter, on cooling, deposites pure mannite in the form of minute acicular crystals, which are often arranged in concentric groups. Mannite differs from sugar, in not fermenting when mixed with water and yeast.

Sugar of Liquorice.—The root of the *Glycyrrhiza glabra*, as also the black extract of the root well known under the name of *liquorice*, contains a saccharine principle; but it is quite distinct from sugar. It may be prepared by infusing the root in boiling water, filtering when cold, and gradually adding sulphuric acid as long as a precipitate, which is a compound of the acid and saccharine matter, is formed. It is first washed with water acidulated with sulphuric acid, and then with pure water; and it is subsequently dissolved in alcohol, which leaves a little vegetable albumen and mucilage. Solution of carbonate of potassa is then added very gradually, so as exactly to neutralize the acid; and after the sulphate of potassa has subsided, the alcoholic solution is decanted and evaporated. It may also be obtained in a similar manner from the extract, except that the solution, when first made, must be purified by white of egg.

Sugar of liquorice is thus procured in the form of a yellow transparent mass, which is unchangeable in the air, and soluble in water and alcohol. It is characterised by its tendency to form sparingly soluble compounds with acids, which accordingly precipitate it from its solution in cold water. It unites also readily with alkaline bases; and when digested in water containing carbonate of potassa, baryta, or lime, carbonic acid is slowly evolved, and a soluble compound of the base with the saccharine matter is generated. (Berzelius.)

Starch or Fecula.—Amidine.

Starch exists abundantly in the vegetable kingdom, being one of the chief ingredients of most varieties of grain, of some roots, such as the potato, and of the kernels of leguminous plants. It is easily procured by letting a small current of water fall upon the dough of wheat-flour enclosed in a piece of linen, and subjecting it at the same time to pressure between the fingers, until the liquid passes off quite clear. The gluten of the flour is left in a pure state, the saccharine and mucilaginous matters are dissolved, and the starch is washed away mechanically, being deposited from the water on standing in the form of a white powder. The starch of commerce is obtained by an analogous process from the grain of wheat and from the potato; but in the preparation of wheat starch, the water containing the soluble and insoluble parts of the grain is allowed to ferment, whereby acetic acid is generated, which dissolves the glutinous portion, and thus facilitates its separation from the starch. The microscopic researches of Raspail have proved that starch, as it exists in plants, occurs as white, shining, but uncrystalline, particles, each of which has its own proper envelope of an amylaceous nature, but more insoluble in water than the interior particles.

Starch is insipid and inodorous, of a white colour, and is insoluble in alcohol, ether, and cold water. It does not crystallize; but it is commonly found in the shops in six-sided columns of considerable regularity, a form occasioned by the contraction which it suffers in drying. Boiling water acts upon it readily, converting it into a tenacious bulky jelly, which is employed for stiffening linen. In a large quantity of hot water, it is dissolved completely, and is not deposited on cooling. The aqueous solution is precipitated by subacetate of oxide of lead; but the best test of starch, by which it is distinguished from all other substances, is iodine. This principle forms with starch, whether solid or in solution, a blue compound which is insoluble in cold water: with hot water it forms a colourless solution, which deposites the blue compound as it cools; but when boiled with water, iodine acts upon the elements of the starch, hydriodic acid is formed, and then on cooling the blue iodide of starch is not reproduced.

Starch unites with the alkalies, forming a compound which is soluble in water, and from which the starch is thrown down by acids. On mixing solutions of starch with baryta, lime, and subacetate of oxide of lead, white insoluble compounds are obtained: and that with oxide of lead, formed at a boiling temperature with excess of the subsalt, contains 72 parts of starch and 28 of oxide of lead. (Berzelius.) Strong sulphuric acid decomposes it. Nitric acid in the cold dissolves starch; but converts it by the aid of heat into oxalic and malic acid.

The effects of heat on starch are peculiar, and have been examined by Caventou. (An. de Chim. et de Ph. xxxi.) On exposing dry starch to a temperature a little above 212° it acquires a slightly red tint, emits an odour of baked bread, and is rendered soluble in cold water; and a similar modification is effected by the action of hot water. Gelatinous starch is generally supposed to be a hydrate of starch; but Caventou maintains that the jelly cannot by any method be restored to its original state. He regards this modified starch as identical with the substance described by Saussure under the name of *amidine*. Saussure thought it was generated by exposing a paste made with starch and water for a long time to the air; but according to Caventou, the amidine was formed by the action of the hot water on starch in making the paste. Its essential character is to yield a blue colour with iodine, and to be soluble in cold water. On gently evaporating the solution to dryness, it becomes a transparent mass like horn, which retains its solubility in cold water.—To torrified starch, that is, to starch thus modified by heat, whether in the dry way or by boiling water, the term *amidine* may be applied.

When starch is exposed to a still higher temperature than is sufficient for its conversion into amidine, a more complete change is effected. It then assumes a reddish-brown colour, swells up and softens, dissolves with much greater facility in cold water, and gives with iodine either a purple colour or none at all. In this state it is very analogous to gum, and is employed by calico-printers under the name of *British gum;* but it differs from real gum in not yielding mucic acid by digestion with nitric acid. A similar change may be produced by long-continued ebullition.

Starch is readily convertible into sugar. This change takes place in seeds during germination, as in the malting of barley; and a similar conversion appears in some instances as an effect of frost, as in the potato, apple, and parsnip. Saccharine matter is also developed when gelatinous starch is kept in a moist state for a long time, either with or without the access of air. If starch is boiled for a considerable time in water acidulated with 1-12th of its weight of sulphuric acid, it is wholly converted into a saccharine matter similar to that of the grape; and this change takes place much more rapidly if the temperature is a few degrees above 212°. This fact was first observed by Kirchoff, and has since been particularly examined by Vogel, De la Rive, and Saussure. It has been established by Saussure that the oxygen of the air exerts no influence over the process, that no gas is disengaged, that the quantity of acid suffers no diminution, that 100 parts of starch yield 110.14 of sugar, and that the only difference in the composition of starch and sugar is, that the latter contains more of the elements of water than the former. He hence inferred that, in Kirchoff's process, the starch is converted into sugar by its elements combining with a certain quantity of oxygen and hydrogen in the proportion to form water; and that the acid acts only by increasing the fluidity of the mass. (Annals of Philosophy, vi.)

The researches of Caventou, already referred to, have thrown considerable light on the chemical nature of several of the amylaceous principles of commerce. The *Indian arrow-root*, which is prepared from the root of the *Maranta arundinacea*, has all the characters of pure starch. Sago, obtained from the cellular substance of an East-Indian palm-tree (*Sagus farinifera*), and tapioca and cassava from the root of the *Iatropha Manihot*, are chemically the same substance. They both exist in the plants from which they are extracted in the form of starch; but as heat is employed in their preparation, the starch is more or less completely converted into amidine. It hence follows that pure potato starch may be used instead of arrow-root; and that the same material, modified by heat, would afford a good substitute for sago and tapioca. Salep, which is obtained from the *Orchis mascula*, consists almost entirely of the substance called *bassorin*, together with a small quantity of gum and starch.

When starch moistened with water is digested with an equal weight of peroxide of manganese, a volatile acid, possessed of an odour similar to hydrocyanic acid, passes over. Its discoverer, M. Tünnermann, who has given it the name of *amylic acid*, considers it a compound of three equivalents of oxygen and two and a half eq. of carbon; but it requires further examination before being enumerated as a distinct acid. (Journal of Science, N. S. iv. 444.)

Gum.

Under this name I include all those immediate vegetable principles which form with water a clammy adhesive solution called *mucilage*, and which when boiled with about four times their weight of nitric acid yield mucic acid. The nitric acid used for the production of mucic acid should have a density of 1.339 at 50° F.

The properties of gum are best studied in pure specimens of gum-arabic, of which it is the principal ingredient. It is colourless, transparent, inodorous, and insipid, and when dry it is very brittle, and has a vitreous fracture. When put into water, either hot or cold, it softens, and then dissolves, constituting mucilage. It is insoluble in ether and alcohol, and the former precipitates gum from its solution in the form of opaque white flakes. Its solubility is increased both by acids and alkalies. Strong sulphuric acid decomposes it, causing the formation of water and acetic acid, with deposition of charcoal. Heated with a quantity of nitric acid insufficient for the production of mucic acid, it yields an acid resembling the malic. The greatest quantity of mucic acid which can be procured from pure gum is 16.88 per cent. (Guerin in An. de Ch. et de Ph. xlix. 248.)

The aqueous solution of gum may be preserved a considerable time without alteration; but at length it becomes sour, and exhales an odour of acetic acid, a change which takes place without exposure to the air, and must, therefore, be owing to a new arrangement of its own elements.

Gum is precipitated from its solution in water by several metallic salts, and especially by subacetate of oxide of lead, which occasions a curdy precipitate, consisting of 38.25 parts of oxide of lead and 61.75 parts of gum. (Berzelius). It is also thrown down by a solution of silicated potassa, but this test is less delicate than the salt of lead.

When gum is heated to redness in close vessels, it yields, in addition to the usual products, a small quantity of ammonia, owing to some impurity, probably gluten, with which it is generally associated.

Gum-Arabic.—This substance is the concrete juice of several species of the *Mimosa* or *Acacia*, natives of Africa and Arabia. It occurs in small, rounded, transparent, friable grains, which are sometimes colourless, and at others yellow, red, or brown. Its density is 1.355. Dried at 250° M. Guerin found it to lose 17.6 per cent. of water: the remaining 82.4 when burned yielded 3 parts of an ash, consisting of the carbonates of lime and potassa, a little phosphate of lime, chloride of potassium, oxide of iron, alumina, silica, and magnesia. When gum-arabic is dissolved in water, a small quantity of insoluble matter containing nitrogen is left, and a portion of it appears to be dissolved in the mucilage. The solution of the gum contains a supermalate of lime, the chlorides of calcium and potassium, and acetate of potassa. (Guerin.) These may be removed by digestion in alcohol.

Gum-Senegal, the juice of the *Acacia Senegalensis*, contains exactly the same principle as gum-arabic. The mucilage of linseed, and probably of most of the mucilaginous seeds and plants, possesses the essential characters of gum-arabic.

Gum-Tragacanth, the juice of the *Astragalus gummifer*, differs essentially from the pure gums. According to Guerin, 100 parts contain 11.1 of water, 2.5 of ashes left when the gum is burned, 53.3 of pure gum soluble in cold water, and identical with that of gum-arabic, and 33.1 of bassorin and starch, which is the part left undissolved by cold water.

The gum which issues from several trees of the genus *Prunus*, as from the peach, plum, apricot, and cherry-tree (*P. Cerasus*), was found by Dr. Bostock to yield mucic acid by the action of nitric acid (Nicholson's Journal, xviii.). M. Guerin finds it to be identical in composition with gum-arabic. It differs, however, in being insoluble in cold water; but when boiled in that liquid, it is dissolved, and the solution has all the characters of pure mucilage. In fact cherry-tree gum, which Guerin distinguishes by the name of *cerasin*, seems isomeric with the standard gum, and acquires identity of character by the mere influence of heat.

The gelatinous principle of fruits, such as is derived from the currant or gooseberry, appears to be very closely allied to gum. It is precipitated from the juice by free admixture with alcohol, forms a mucilaginous solution with water, though less adhesive than gum, is neutral to test paper, and with nitric acid yields mucic and oxalic acids. It is distinguished however from pure gum by being instantly converted into pectic acid by the presence of a fixed alkali or alkaline earth: on adding potassa, and then an acid, a jelly falls, possessed of all the characters of pectic acid; and when baryta is employed, a pectate of baryta subsides. The jelly of fruits is thus distinct from gum, and Braconnot, by whom these facts were observed, proposes for it the name of *pectin*. (An. de Ch. et de Ph. xlvii. 266.)

Lignin.

Lignin, or *woody fibre* constitutes the fibrous structure of vegetable substances, and is the most abundant principle in plants. The different kinds of wood contain about 96 per cent. of lignin. It is prepared by digesting the sawings of any kind of wood successively in alcohol, water, and dilute hydrochloric acid, until all the substances soluble in these menstrua are removed.

Lignin has neither taste nor odour, undergoes no change by keeping, and is insoluble in alcohol, water, and the dilute acids. By digestion in a concentrated solution of pure potassa, it is converted according to Braconnot into a substance similar to ulmin. Mixed with strong sulphuric acid it suffers decomposition, and is changed into a matter resembling gum; and on boiling the liquid for some time the mucilage disappears, and a saccharine principle like the sugar of grapes is generated. Braconnot finds that several other substances which consist chiefly of woody fibre, such as straw, bark, or linen, yield sugar by a similar treatment. (An. de Ch. et de Ph. xii.) Digested in nitric acid, lignin is converted into the oxalic, malic, and acetic acids.

SECTION IV.

OLEAGINOUS, RESINOUS, AND BITUMINOUS SUBSTANCES.

The compounds included in this section, besides being otherwise allied, are remarkable for their combustibility, and supply the materials used in the arts for the production of heat and light. Most of them contain a much larger quantity of hydrogen than suffices for forming water with their oxygen. They exert in general but a very feeble affinity for other bodies, and consequently their combining weights and atomic constitution have in few instances been determined. Their composition will, therefore, be best stated in reference to 100 parts, as in the following table:—

Substances.	Carbon.	Hyd.	Oxygen.	Analyzed by
Olive oil	77.213	13.36	9.427	Gay-Lussac and Thenard.
Essence of turpentine Oil of lemons	85.5	11.5		Dumas.
Camphor	79.28	10.36	10.36	Dumas.
Do. from oil of peppermint.	77.3	12.6	10.1	Dumas.
Do. from oil of anise	81.4	7.98	10.62	Dumas.
Oil of cloves	70.02	7.42	22.56	Dumas.
Caryophylline	79.27	10.36	10.37	Dumas.
Oil of bitter almonds	79·56	5.56	14.88	Liebig and Wohler.
Common resin	75.944	10.719	13.337	Gay-Lussac and Thenard.
Caoutchouc	90	9.12	0.88	Ure.
Bees-wax	80.4	11.3	8.3	Ure.

OLEAGINOUS SUBSTANCES.

Oils are characterized by a peculiar unctuous feel, by inflammability, and by insolubility in water. They are divided into the fixed and volatile oils, the former of which are comparatively fixed in the fire, and, therefore, give a permanently greasy stain to paper; while the latter, owing to their volatility produce a stain which disappears by gentle heat.

FIXED OILS.

The fixed oils are usually contained in the seeds of plants, as for example in the almond, linseed, rape-seed, and poppy-seed; but olive-oil is extracted from the pulp which surrounds the stone. They are procured by bruising the seed, and subjecting the pulpy matter to pressure in hempen bags, a gentle heat being generally employed at the same time to render the oil more limpid.

Fixed oils are nearly inodorous, have little taste, and are lighter than water, their density in general varying from 0.9 to 0.96. Some, such as cocoa-nut and palm-oil, are fixed at 50° or 60°; but most of them are fluid at common temperatures, and they all become limpid in becoming warm. They are commonly of a yellow colour, but may be rendered nearly or quite colourless by the action of animal charcoal. At or near 600° they begin to boil, but suffer partial decomposition at the same time, an inflammable vapour being disengaged even below 500°. When heated to redness in close vessels, a large quantity of the combustible compounds of carbon and hydrogen are formed, together with the other products of the destructive distillation of vegetable substances; and in the open air they burn with a clear white light, and formation of water and carbonic acid. They may hence be employed for the purposes of artificial illumination, as well in lamps, as for the manufacture of gas.

Fixed oils undergo considerable change by exposure to the air, a change owing to the action of oxygen, and which has been examined into by Saussure (An. de Ch. et de Ph. xlix. 225). Olive-oil, recently expressed, was confined over mercury in a tube full of oxygen gas, and underwent no appreciable alteration during the first five months, absorbing only about its own volume of oxygen: the absorption then became very rapid, so that at the end of the first year it had absorbed 41 times its volume of oxygen, and became quite colourless; and at the close of the fourth year, when the action had become very slight, the whole absorption of oxygen amounted to 102 times its volume. The oil at that period was very rancid, and less limpid than at first. During these changes the oil gave out 22 times its volume of carbonic acid and about 6 of hydrogen, together with a trace of carbonic oxide. The rancidity of oils is commonly ascribed to the mucilaginous matters which they contain becoming acid, and probably the first change is of this nature; but subsequently, when the principal absorption takes place, the oil itself appears to be modified.

Similar changes occur to a much greater extent with linseed-oil and other *siccative* oils, which owe their property of *drying* to the absorption of oxygen. The oil of hemp-seed, recently expressed, was exposed for a month to oxygen gas, and absorbed of it less than its own volume: there was no absorption during the second month; but subsequently the absorption became rapid, and at the end of one year the oil had taken up 155 times its volume of oxygen. At the time of the absorption becoming rapid, the oil lost its colour, and its surface acquired a mucilaginous pellicle. During the three following years it still continued to absorb oxygen, and to become viscid: at the end of that time it had evolved about 24 times its bulk of carbonic acid, and 7 of hydrogen, with a little carburetted hydrogen. The oil of walnuts gave similar results. This property of drying, for which linseed oil is is remarkable, may be communicated quickly by heating the oil in an open vessel. Drying oils are used for making oil paint, and mixed with lampblack they constitute printers' ink.

The absorption of oxygen by fixed, and especially by drying oils, is under some circumstances so abundant and rapid, and accompanied with so much heat, that light porous combustible materials, such as lampblack, hemp, or cotton-wool, may be kindled by it. Substances of this kind, moistened with linseed-oil, have been known to take fire during the space of 24 hours, a circumstance which has repeatedly been the cause of extensive fires in warehouses and in cotton manufactories.

Fixed oils do not unite with water, but they may be permanently suspended in that fluid by means of mucilage or sugar, so as to constitute an *emulsion*. They are for the most part very sparingly soluble in alcohol and ether. Strong sulphuric acid thickens the fixed oils, and forms with them a tenacious matter like soap; and they are likewise rendered thick and viscid by the action of chlorine. Concentrated nitric acid acts upon them with great energy, giving rise in some instances to the production of flame.

Alkaline bases have a remarkable action on oils and fats. With ammonia oil forms a soapy liquid to which the name of *volatile liniment* is applied: it is a direct compound of the oil and alkali suspended in water; but by keeping, an ammoniacal soap is generated. The pure fixed alkalies act similarly in the cold; but when heated with oil, the latter undergoes an entire change of constitution, and soap is generated. A similar action is occasioned by most of the metallic oxides.

The elaborate researches of Chevreul on the nature of oils and fats have shown that these bodies are not pure proximate principles, but compounds in variable proportion of at least two other compounds, one of which is solid at common temperatures, while the other is fluid. To the former he applied the name of stearine, from *στεαρ suet*, and to the latter *elaine* or *oleine*, from *ελαιον oil*. Oleine is the fluid principle of oils, and gives fluidity to those oils in which it predominates. It requires a cold of 20° for congelation, and is prepared from oils by exposing them to a cold of about 25°, and pressing the congealed mass between folds of bibulous paper; when the oleine is absorbed, and may be separated by pressing the paper under water. Oleine is well adapted for lubricating the wheels of watches or other delicate machinery, since it does not thicken or become rancid by exposure to the air. From late experiments by Lecanu, it appears that stearine, though contained in animal fats, is rarely present in those of vegetable origin: the solid principle present in the latter is *margarine*, a substance analogous in its properties to stearine. The nature of these substances, as well as the changes induced in them during the formation of soap, will be considered in the section on the animal fats.

VOLATILE OR ESSENTIAL OILS.

Aromatic plants owe their flavour to the presence of a *volatile* or *essential* oil, which may be obtained by distillation, water being put into the still along with the plant in order to prevent the latter from being burned. The oil and water pass over into the recipient, and the oil collects at the bottom or the surface of the water according to its density.

Essential oils have a penetrating odour and acrid taste, which are often pleasant when sufficiently diluted. They are soluble in alcohol, though in different proportions. They are sparingly dissolved by water, and hence water acquires the odour of the oil with which it is distilled. With the fixed oils they unite in every proportion, and are sometimes adulterated with them, an imposition easily detected by the mixed oil causing on paper a greasy stain which is not removed by heat.

Volatile oils burn in the open air with a clear white light, and the sole products of the combustion are water and carbonic acid. On exposure to the atmosphere, they gradually absorb a large quantity of oxygen, in consequence of which they become thick, acquire a deep yellowish-brown colour, and are at length converted into a substance resembling resin. Some of them deposite during this action crystalline compounds of a definite nature. Saussure has shown that, as with fixed oils, carbonic acid and hydrogen gases are emitted at the same time. This change is rendered more rapid by the agency of light.

Of the acids, the action of strong nitric acid on volatile oils is the most energetic, being often attended with vivid combustion,—an effect which is rendered more certain by previously adding to the nitric a few drops of sulphuric acid.

Volatile oils do not unite readily with metallic oxides, and are attacked with difficulty even by the alkalies. The substance called Starkey's soap is made by triturating oil of turpentine with an alkali.

Volatile oils dissolve sulphur in large quantity, forming a deep brown-coloured liquid, called *balsam of sulphur*. The solution is best made by boiling flowers of sulphur in spirit of turpentine. Phosphorus may likewise be dissolved by the same menstruum.

The following table contains a list of the principal essential oils:—

Oils of	Colour.	Density.
Turpentine	colourless	0.87
Lemons	colourless or pale yellow	0.85
Anise	do. do.	0.9857 at 80°
Juniper	do. or greenish-yellow	0.911
Chamomile	deep blue	
Carraway	pale yellow	0.94
Lavender	yellow	0.877 to 0.898
Peppermint	colourless or pale yellow	0.92
Rosemary	colourless	0.89 to 0.92
Camphor	white	0.986
Cinnamon	yellow	1.035
Cloves	colourless or pale yellow	1.061
Sassafras	yellow or red	1.094
Mustard	yellow	1.0387
Bitter almonds	colourless	1.043

The essential oils differ in constitution from the fixed oils, and are divisible into three groups. The first consists of the essence of turpentine and of lemons, which are composed solely of carbon and hydrogen; the second, which includes oil of anise and the ten following oils, together with the solid essence, camphor, contain carbon, hydrogen, and oxygen; and the oils of the third group, as oil of mustard and bitter almonds, contain some other element in addition to the foregoing.

Essence of Turpentine.—This oil, which is the most common and most generally used of all the essential oils, is procured by distillation from common turpentine, and is a limpid colourless fluid, which may be distilled without residue, and yields a dense white light in burning. It is sparingly soluble in alcohol. In its purest form it is a definite compound of carbon and hydrogen, which has already been described under the name of camphene (page 255). But the specimens met with in commerce invariably contain oxygen, owing to the absorption of that gas from the atmosphere, whereby changes in the constitution of the essence are produced. It is not improbable, also, that the essence obtained from different kinds of turpentine may differ in original constitution.

Essence of turpentine or camphene forms an interesting compound with hydrochloric acid, called artificial camphor, the composition of which was stated at page 255. It is formed by transmitting a current of perfectly dry hydrochloric acid gas through oil of turpentine, which has been recently and carefully distilled, surrounded by a mixture of snow and salt: a quantity of gas is absorbed equal to one-third of the weight of the oil; the liquid acquires a deep brown colour; and a white crystalline volatile substance, very similar to camphor, is slowly generated. The liquid parts should be removed by pressure between folds of bibulous paper. This matter was discovered by Kind, and has since been studied by Trommsdorf, Gehlen, Thenard, and Dumas. When carefully separated from adhering acid by washing with water containing a little carbonate of soda, it is quite neutral, and affords an instance of a carburet of hydrogen acting as a base to a strong acid.

The oil of lemons has the same composition as that of turpentine (page 539), and forms with hydrochloric acid an artificial camphor analogous to the foregoing.

Camphor.—This substance exists ready formed in the *Laurus Camphora* of Japan, and is obtained from its trunk, root, and branches by sublimation. It has a bitterish, aromatic, pungent taste, accompanied with a sense of coolness. It is unctuous to the touch, and rather brittle, though possessing a degree of toughness which prevents it from being pulverized with facility; but it is easily reduced to powder by trituration with a few drops of alcohol. Its specific gravity is 0.988. It is exceedingly volatile, being gradually dissipated in vapour if kept in open vessels. At 288° it enters into fusion, and boils at 400°. It is insoluble in water; but when triturated with sugar, and then mixed with that fluid, a portion is dissolved sufficient for communicating its flavour. It is dissolved freely by alcohol, and is thrown down by the addition of water. It is likewise soluble in the fixed and volatile oils, and in strong acetic acid. Sulphuric acid decomposes camphor, converting it into a substance like artificial tannic acid. (Mr. Hatchett.)

The researches of Dumas have shown (page 256) that camphor is the oxide of camphene, and that the same inflammable compound by the action of nitric acid is still further oxidized, and then constitutes camphoric acid. He has gone far to prove that the essential oils of the second group are solutions in variable proportion of camphor in liquid carburets of hydrogen. The latter seem to be the essential and original material of the oil, which by a subsequent process of oxidation yields more or less camphor. From the oil of peppermint exposed to a cold of 32°, and then compressed in bibulous paper to separate adhering oil, he obtained a volatile crystalline solid like camphor, the composition of which is reducible to the formula $C^{10}H^{10}+O$. A similar substance was procured by congelation from oil of anise, the formula of which is $C^{10}H^{6}+O$. Analogous camphors may be procured from most of the essential oils, if kept for some time in a partially closed bottle. By a more complete oxidation, the same compound radicals give rise to resinous matter.

Oil of Cloves.—Dumas finds that the dense volatile oils are more highly oxidized than the lighter ones, and are disposed to act as acids in relation to alkaline bases. He obtained a definite crystalline compound of the oil of cloves with ammonia, composed of 175.4 parts or one eq. of the oil, and 17.15 parts or one eq. of the alkali. The elements of the oil are in the ratio of 122.4 parts or twenty eq. of carbon, 13 parts or thirteen eq. of hydrogen, and 40 parts or five eq. of oxygen, the formula being $C^{20}H^{13}+5O$. The crystalline solid, called *caryophylline*, deposited from this oil by keeping, has the same composition as camphor.

Oil of Mustard.—This oil differs from the foregoing in containing sulphur and nitrogen. Dumas and Pelouze found 100 parts of the oil to consist of sulphur 20.25, nitrogen 14.45, hydrogen 5.02, carbon 49.98, and oxygen 10.3. The carbon, hydrogen, and nitrogen form, they conceive, a distinct compound radical, which then combines with sulphur and oxygen; but their investigation on the subject is not yet fully reported. (An. de Ch. et de Ph. liii. 184.)

Oil of Bitter Almonds.—Benzule.

This oil differs from all the preceding oils, and has lately led to important discoveries. When the bitter almond is reduced to a pulp and subjected to compression, a pure fixed oil is obtained; but when distilled along with water, a volatile poisonous oil passes over, which smells strongly of hydrocyanic acid, and contains a volatile oil, mixed or combined with that acid. Neither the volatile oil nor hydrocyanic acid pre-exist in the almond, but are developed in it by the action of water during the distillation. By mixing the impure oil with a solution of potassa and protochloride of iron, agitating strongly, and distilling the mixture, the oil is obtained quite free from hydrocyanic acid; and by a second distillation from pulverized lime it is deprived of adhering moisture.

The oil thus purified is a colourless volatile liquid, which retains its original odour, has a burning aromatic taste, and a density of 1.043. It is sparingly soluble in water, but freely by alcohol. When suddenly and strongly heated in open vessels, it takes fire and burns with flame; but it may be passed alone through a red-hot glass tube without decomposition. In examining its properties and composition, Liebig and Wöhler have proved that it may be regarded as a compound of hydrogen with a substance called benzule (page 513), which consists of 85.68 parts or fourteen eq. of carbon, 5 parts or five eq. of hydrogen, and 16 parts or two eq. of oxygen. The formula of benzule is $C^{14}H^{5}O^{2}$, and its symbol is Bz. Benzule has not yet been obtained in an uncombined state; but it is readily transferable without decomposition from one element to another in the same manner as cyanogen. The several compounds examined by Liebig and Wöhler are thus constituted:—(An de Ch. et de Ph. li. 273.)

Names.	1 eq. Benzule.		Equiv.	Formulæ.
Hyduret of benzule	106.68 + Hydrogen	1	1 eq. = 107.68	Bz + H.
Anhydrous benzoic acid	106.68 + Oxygen	8	1 eq. = 114.68	Bz + O or $\dot{Bz}$
Chloride of benzule	106.68 + Chlorine	35.42	1 eq. = 142.1	Bz + Cl.
Bromide do.	106.68 + Bromine	78.4	1 eq. = 185.08	Bz + Br.
Iodide do.	106.68 + Iodine	126.3	1 eq. = 232.98	Bz + I.
Sulphuret do.	106.68 + Sulphur	16.1	1 eq. = 122.78	Bz + S.
Cyanuret do.	106.68 + Cyanogen	26.39	1 eq. = 133.07	Bz + Cy.

The purified oil is a hyduret of benzule. When heated with hydrate of potassa, the oil interchanges elements with the water, so that

1 eq. oil	Bz+H	yield	1 eq. anhydrous benzoic acid	Bz+O
and 1 eq. water	H+O		and 2 eq. of hydrogen	2H;

the hydrogen is evolved and benzoate of potassa is left. When exposed to the air or pure oxygen gas the reaction is such that

1 eq. oil	Bz+H	yield	1 eq. anhydrous benzoic acid	Bz+O
and 2 eq. oxygen	2O		and 1 eq. water . .	H+O;

and these products constitute one eq. of crystallized benzoic acid.

Chloride of Benzule.—Hyduret of benzule absorbs chlorine gas with heat, hydrochloric acid and chloride of benzule are generated, and the latter, after being heated to expel any excess of chlorine, remains as a limpid liquid like water. It has a density of 1.196, a peculiar pungent odour, irritates the eyes, and boils at an elevated temperature. It is insoluble in water; but by long ebullition with water, it yields hydrochloric and benzoic acids. It may be distilled from anhydrous lime or baryta without decomposition; but when heated with hydrate of potassa, it yields chloride of potassium and benzoate of potassa.

Bromide of Benzule.—It is formed by the action of bromine on hyduret of benzule; and after expelling the excess of bromine by heat, the bromide is left as a soft semi-fluid mass, consisting of large foliated crystals of a brown colour. It is soluble without change in alcohol and ether. By long boiling with water, it is converted into hydrobromic and benzoic acids.

The *iodide of benzule* is obtained as a brown liquid by distilling a mixture of iodide of potassium with chloride of benzule, and on cooling becomes a crystalline solid of the same colour. When free from mixed iodine it is colourless, and resembles the bromide in its chemical relations.

Sulphuret of Benzule.—It is formed by distilling chloride of benzule with sulphuret of lead in fine powder, and passes over as an oil-like fluid, which on cooling becomes a soft crystalline solid of a yellow colour. Its odour resembles that of sulphur. It is not changed by the action of water, and is but slowly resolved by a boiling solution of potassa into benzoate of potassa and sulphuret of potassium.

Cyanuret of Benzule.—It is obtained by distilling the chloride of benzule with bicyanuret of mercury, and collects in the recipient as an oily fluid of a yellow colour. By distillation it is rendered colourless, but the yellow colour quickly returns. Its vapour has a strong penetrating odour, and irritates the eyes. By water, in which it is otherwise insoluble, it is speedily converted into hydrocyanic and benzoic acids.

Benzamide.—Chloride of benzule has the property of absorbing, with much heat, dry ammoniacal gas, and of forming a white solid, which, after complete saturation with ammonia, consists solely of hydrochlorate of ammonia and *benzamide.* By cold water the former is dissolved, and the latter insulated. It derives its name from the fact that it bears to benzoate of ammonia the same relation as oxamide to oxalate of ammonia (page 500).

Pure benzamide fuses at 239° into a limpid liquid, which concretes into a foliated mass on cooling. When strongly heated it boils, and passes over unchanged. It is very sparingly dissolved by cold water, but readily and without decomposition in boiling water. It is very soluble in alcohol, and is dissolved by boiling ether. By evaporation from its solutions it crystallizes in right rhomboidal prisms of a pearly lustre. With a solution of potassa in the cold it is not changed, and emits no odour of ammonia; but when boiled with the alkaline solution, ammonia is disengaged, and benzoate of potassa is found in solution. The same change is effected by boiling it in a solution of sulphuric acid.

In the action of ammonia on chloride of benzule

$$\begin{array}{lll} \text{1 eq. chloride} & C^{14}H^{5}O^{2}+Cl & \multirow{2}{*}{\text{yield}} \left\{ \begin{array}{l} \text{1 eq. hydrochlorate of ammonia} \\ \qquad\qquad H^{3}N+HCl \end{array} \right. \\ \text{and 2 eq. ammonia} & 2\,(3H+N) & \quad \text{and 1 eq. benzamide } C^{14}H^{5}O^{2}+H^{2}N. \end{array}$$

It is obvious that

$$\begin{array}{llcll} \text{1 eq. benzamide} & C^{14}H^{5}O^{2}+H^{2}N & \text{yield} & \text{1 eq. anhyd. benzoic acid} & C^{14}H^{5}O^{2}+O \\ \text{and 1 eq. water} & H+O & & \text{and 1 eq. ammonia} & 3H+N. \end{array}$$

I have theoretically represented benzamide as a compound of benzule with dinituret of hydrogen; but other hypotheses may be formed respecting its constitution, [illegible] in the case of oxamide.

Benzoine.—The oil of bitter almonds, like several other essential oils, has been observed to deposite a crystalline matter, which is formed abundantly when the oil is left for a few weeks in a corked bottle in contact with a strong solution of potassa. It has at first a yellow tint; but by solution in boiling alcohol, and digestion with animal charcoal, it may be obtained pure and white. It crystallizes from its alcoholic solution in transparent prismatic crystals, which fuse at 248°, and may be distilled without change. It has neither taste nor odour. Liebig and Wöhler found its elements to coincide exactly with those of the original oil which yielded it, though doubtless their arrangement is very different.

Coumarin.—This name was first applied to the odoriferous principle of the Tonka bean by M. Guibourt, and has since been adopted by MM. Boullay and Boutron-Charlard. (Journ. de Pharmacie, 1825.) It is derived from the term *Coumarouna odorata*, given by Aublet to the plant which yields the bean.

Coumarin is white, of a hot pungent taste, and distinct aromatic odour. It crystallizes sometimes in square needles, and at other times in short prisms. It is moderately hard, fracture clean, lustre considerable, and density greater than that of water. It fuses at a moderate temperature into a transparent fluid, which yields an opaque crystalline mass on cooling. Heated in close vessels, it is sublimed without change. It is sparingly soluble in water; but is readily dissolved by ether and alcohol, and the solutions crystallize by spontaneous evaporation. It is very soluble in fixed and volatile oils.

Vogel mistook coumarin for benzoic acid: Boullay and Boutron-Charlard maintain that it has neither an acid nor alkaline reaction, and that it is a peculiar independent principle, nearly allied to the essential oils. These chemists did not find any benzoic acid in the Tonka bean, and consider coumarin as the sole cause of its odour.

RESINOUS SUBSTANCES.

Resins.—Resins are the inspissated juices of plants, and commonly occur either pure or in combination with an essential oil. They are solid at common temperatures, brittle, inodorous, and insipid. They are non-conductors of electricity, and when rubbed become negatively electric. They are generally of a yellow colour, and semi-transparent.

Resins are fused by the application of heat, and by a still higher temperature are decomposed. In close vessels they yield empyreumatic oil, and a large quantity of carburetted hydrogen, a small residue of charcoal remaining. In the open air they burn with a yellow flame and much smoke, being resolved into carbonic acid and water.

Resins are dissolved by alcohol, ether, and the essential oils, and the alcoholic and ethereal solutions are precipitated by water, a fluid in which they are quite insoluble. Their best solvent is pure potassa and soda, and they are also soluble in the alkaline carbonates by the aid of heat. The product is in each case a soapy compound, which is decomposed by an acid.

Concentrated sulphuric acid dissolves resins; but the acid and the resin mutually decompose each other, with disengagement of sulphurous acid, and deposition of charcoal. Nitric acid acts upon them with violence, converting them into a species of tannin, which was discovered by Mr. Hatchett. No oxalic acid is formed during the action.

The uses of resin are various. Melted with wax and oil, resins constitute ointments and plasters. Combined with oil or alcohol, they form different kinds of oil and spirit varnish. Sealing-wax is composed of lac, Venice turpentine, and common resin. The composition is coloured black by means of lampblack, or red by cinnabar or red lead. Lampblack is the soot of imperfectly burned resin.

Of the different resins the most important are common resin, copal, lac, sandarach, mastich, elemi, and dragon's blood. The first is procured by heating turpentine, which consists of oil of turpentine and resin, so as to expel the volatile oil. The common turpentine obtained by incisions made in the trunk of the Scotch fir-tree (*Pinus sylvestris*) is employed for this purpose; but the other kinds of turpentine, such as Venice turpentine, that from the larch (*Pinus larix*), Canadian turpentine from the *Pinus balsamea*, or the Strasburgh turpentine from the *Pinus picea*, yield resin by a similar treatment.

When turpentine is extracted from the wood of the fir-tree by heat, partial decomposition ensues, and a dark substance, consisting of resin, empyreumatic oil, and acetic acid is the product. This constitutes tar; and when inspissated by boiling, it forms pitch. Common resin fuses at 276°, is completely liquid at 306°, and at about 316° bubbles of gaseous matter escape, giving rise to the appearance of ebullition. By distillation it yields empyreumatic oils: in the first part of the process a limpid oil passes over, which rises in vapour at 300°, and boils at 360°; but subsequently the product becomes less and less limpid, till towards the close it is very thick. This matter becomes limpid when heat is applied, and boils at about 500° F. At a red heat resin is entirely decomposed, yielding a large quantity of combustible gas, which is employed for the purpose of artificial illumination.

Amber.—This substance is brought chiefly from the southern coast of the Baltic, occurring sometimes in beds of bituminous wood, and at others on the shore, being doubtless washed out from strata of brown coal by the action of water. Its vegetable origin is amply attested by the substances with which it is associated, by its resinous nature, and by the vegetable matters which it frequently envelopes. It is commonly met with in translucent pieces of various shades of yellow and brown; but it is sometimes transparent. Its specific gravity varies from 1.065 to 1.07. It may be regarded as a mixture of several substances; namely, a volatile oil, succinic acid, separable like the former by heat, two different modifications of resin both soluble in alcohol and ether, and a peculiar bituminous matter, which is insoluble in alcohol and ether, and is the most abundant principle in amber. (Berzelius.)

Balsams.—The balsams are native compounds of resin and benzoic acid, and issue from incisions made in the trees which contain them, in the same manner as turpentine from the fir. Some of them, such as storax and benzoin, are solid; while others, of which the balsams of Tolu and Peru are examples, are viscid fluids.

Gum-resins.—The substances to which this name is applied are the concrete juices of certain plants, and consist of resin, essential oil, gum, and extractive vegetable matter. The two former principles are soluble in alcohol, and the two latter in water. Their proper solvent, therefore, is proof spirit. Under the class of gum-resins are comprehended several valuable medicines, such as aloes, ammoniacum, assafœtida, euphorbium, galbanum, gamboge, myrrh, scammony, and guaiacum.

Caoutchouc, commonly called elastic gum or Indian rubber, is the concrete juice of the *Hævea caoutchouc* and *Iatropa elastica*, natives of South America, and of the *Ficus Indica* and *Artocarpus integrifolia*, which grow in the East Indies. It is a soft yielding solid, of a whitish colour when not blackened by smoke, possesses considerable tenacity, and is particularly remarkable for its elasticity. It is inflammable, and burns with a bright flame. It is insoluble in water and alcohol; but it dissolves, though with some difficulty, in pure ether. It is very sparingly dissolved by the alkalies, but its elasticity is destroyed by their action. By the sulphuric and nitric acids it is decomposed, the former causing deposition of charcoal, and the latter formation of oxalic acid.

Caoutchouc is soluble in the essential oils, ether, naphtha, cajeput oil, and in the volatile liquid obtained by distilling caoutchouc; and from all these solvents, except the essential oils, it is left on evaporation without loss of its elasticity. Before actually dissolving, the caoutchouc swells up remarkably, and acquires a soft gelatinous aspect and consistency: in this state it is used for rendering cloth and leather impervious to water, and, as suggested by Dr. Mitchell of Philadelphia, may be cut with a wet knife into thin sheets or bottles, and be extended to a great size.*

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* Dr. Mitchell has favoured me with the following detailed description of his peculiar mode of preparing bags of caoutchouc of large size:—"Soak the common bags in sulphuric ether, sp. gr. 0.753, at a temperature not less than 50° Fahr. for a period of time not less than one week (the longer the better). Empty the bag, wipe it dry, put into it some dry powder, such as starch, insert a tube into the neck, and fasten it by a broad soft band slightly applied, and then commence by mouth or bellows the inflation. If the bag be unequal in thickness, restrain by the hand the bulging of the thinner

When caoutchouc is cautiously heated, it fuses without decomposition; but at a higher temperature it is resolved into a volatile liquid of a brown colour, which amounts to 8-10ths of the original caoutchouc. When carefully rectified, a very volatile liquid of sp. gr. 0.64 is obtained, which is very combustible and burns with a bright flame, mingles with alcohol, and dissolves copal and other resins. It is manufactured in large quantity by Messrs. Enderby, of London, and is very useful as a solvent for caoutchouc and for the preparation of varnishes.

Wax.—This substance, which partakes of the nature of a fixed oil, is an abundant vegetable production, entering into the composition of the pollen of flowers, covering the envelope of the plum and other fruit, especially the berries of the *Myrica cerifera*, and in many instances forming a kind of varnish to the surface of leaves. From this circumstance it was long supposed that wax is solely of vegetable origin, and that the wax of the honeycomb is derived from flowers only; but it appears from the observations of Huber that it must likewise be regarded as an animal product, since he found bees to deposite wax, though fed on nothing but sugar. Consistently with this remark it has been proved by Oppermann that pure vegetable wax differs from bees-wax in the ratio of its elements. (An. de Ch. et de Ph. xlix. 240.)

Common wax is always more or less coloured, and has a distinct peculiar odour, of both which it may be deprived by exposure in thin slices to light, air, and moisture, or more speedily by the action of chlorine. At ordinary temperatures it is solid, and somewhat brittle; but it may easily be cut with a knife, and the fresh surface presents a characteristic appearance, to which the name of waxy lustre is applied. Its specific gravity is 0.96. At about 150° it enters into fusion, and boils at a high temperature. Heated to redness in close vessels it suffers complete decomposition, yielding products very similar to those which are procured under the same circumstances from oil. As it burns with a clear white light, it is employed for forming candles.

Wax is insoluble in water, and is only sparingly dissolved by boiling alcohol or ether, from which the greater part is deposited on cooling. It is readily attacked by the fixed alkalies, being converted into a soap which is soluble in hot water; and according to Pfaff, the action is attended, as in oils, with the formation of an acid, to which the name of *ceric acid* is applied. It unites by the aid of heat in every proportion with the fixed and volatile oils, and with resin. With different quantities of oil it constitutes the simple liniment, ointment, and cerate of the Pharmacopœia.

Wax, according to the observations of John, consists of two different principles, one of which is soluble, and the other insoluble in alcohol. To the former he has given the name of *cerin*, and to the latter of *myricin*. It has been thought that these principles are generated in the wax by the alcohol used in separating them; but the opinion of John is supported by a fact mentioned to me by Dr. Christison, namely, that the suetty matter of the cinnamon berry consists, with the exception of a little oil, entirely of cerin, without any myricin.

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parts, until the thicker have been made to give way a little. When the bag has become by such means nearly uniform, inflate a little more, shake up the included starch, and let the bag collapse. Repeat the inflation, and carry it to a greater extent, again permit the collapse, again inflate still more extensively, and so on, until the bag is sufficiently distended. Mere gas holders are thus easily made, but it requires some dexterity and experience to make them thin enough for balloons. The whole experiment should not occupy more than from five to twenty minutes of time; and the prepared bag should be closed and hung up to dry for a day or two."—*Ed.*

BITUMINOUS SUBSTANCES.

Under this title are included several inflammable substances which, though of vegetable origin, are found in the earth, or issue from its surface. They may be conveniently arranged under the two heads of bitumen and pit-coal. The first comprehends *naphtha*, *petroleum*, *mineral tar*, *asphaltum*, *mineral pitch*, and *retinasphaltum*, of which the three first mentioned are liquid, and the others solid. The second comprises *brown coal*, the different varieties of *common or black coal*, and *glance coal*.

BITUMEN.

The characters of *naphtha*, the purest form of bitumen, have already been described (page 252).

Petroleum is much less limpid than naphtha, has a reddish-brown colour, and is unctuous to the touch. It is found in several parts of Britain and the continent of Europe, in the West Indies, and in Persia. It occurs particularly in coal districts. *Mineral tar* is very similar to petroleum, but is more viscid and of a deeper colour. Both these species become thick by exposure to the atmosphere, and in the opinion of Mr. Hatchett pass into solid bitumen.

Asphaltum is a solid brittle bitumen, of a black colour, vitreous lustre, and conchoidal fracture. It melts easily, and is very inflammable. It emits a bituminous odour when rubbed, and by distillation yields a fluid like naphtha. It is soluble in about five times its weight of naphtha, and the solution forms a good varnish. It is rather denser than water.

Asphaltum is found on the surface and on the banks of the Dead Sea, and occurs in large quantity in Barbadoes and Trinidad. It was employed by the ancients in building, and is said to have been used by the Egyptians in embalming.

Mineral Pitch or *Maltha* is likewise a solid bitumen, but is much softer than asphaltum. Elastic bitumen, or *mineral caoutchouc*, is a rare variety of mineral pitch, found only in the Odin mine, near Castleton in Derbyshire.

Retinasphaltum is a peculiar bituminous substance, found associated with the brown coal of Bovey in Devonshire (Phil. Trans. 1804). It consists partly of bitumen, and partly of resin, a composition which led Mr. Hatchett to the opinion that bitumens are chiefly formed from the resinous principle of plants.

Inflammable Principles of Tar.

Among the products of the destructive distillation of vegetable and animal substances is a black inflammable liquid called *tar*, which in aspect resembles the tar from fir (page 546). A large quantity is formed during the distillation of wood, and in the preparation of coal gas. The tar obtained from such sources has been the subject of an elaborate inquiry by Dr. Reichenbach, of Blansko, who has discovered in it no fewer than six new principles; namely, *paraffine*, *eupione*, *creosote*, *picamar*, *capnomor*, and *pittacal*. A description of the two former will be found at pages 251–2, and the latter will be described in this place. The original essays of Reichenbach appeared in Schweigger-Seidel's Journal for 1830 and the following years.

Creosote.—This substance exists in solution in crude pyroligneous acid; but it is best prepared from those portions of the oil distilled from wood-tar, which are heavier than water. The oil is first freed from adhering acetic acid by carbonate of potassa, and, after separation from the acetate, is distilled. A little phosphoric acid is mixed with the product to neutralize ammonia, and another distillation resorted to. It is next mixed with a strong solution of potassa, which combines with creosote, allows any eupione which may be present to collect on its surface, and by digestion decomposes other organic matter: the alkaline solution is then neutralized by sulphuric acid, and the oil which separates is collected and distilled. For the complete purification of the creosote, this treatment with potassa, followed by neutralization and distillation, requires to be frequently repeated.

Creosote is a colourless transparent liquid of an oily consistence, which retains its fluidity at —17°, has a sp. gr. of 1.037 at 68°, boils at 397°, is a non-conductor of electricity, and refracts light powerfully. It has a burning taste followed by sweetness, and its odour is like that of wood-smoke or rather of smoked meat. It is highly antiseptic to meat: the antiseptic virtue of tar, smoke, and crude pyroligneous acid seems owing to the presence of creosote. Its name, from κρέας *flesh*, and σώζω *I save*, was suggested by this property.

Creosote requires about 80 parts of water for solution, and is soluble in every proportion in alcohol, ether, sulphuret of carbon, eupione, and naphtha. It has neither an acid nor alkaline reaction with test-paper, but combines both with acids and alkalies. With potassa, soda, lime, and baryta it forms compounds soluble in water; but the creosote is separated even by feeble acids. Of the acids, it unites most readily with the acetic, dissolving in every proportion: by strong nitric and sulphuric acid it is decomposed. Creosote unites also with chlorine, iodine, bromine, sulphur, and phosphorus.

Creosote acts powerfully in coagulating albumen, this effect being produced by a solution of one drop in a large quantity of water. It acts with energy on living beings. Insects and fish thrown into the aqueous solution of creosote are killed, and plants die when watered with it. It appears useful in medicine: it is said to be very efficacious as a topical application in toothach, ulcers, and cutaneous diseases; and it probably admits of many other applications.

Creosote is a compound of carbon, hydrogen, and oxygen, but the ratio of its elements is not yet known.

Picamar.—This substance is the bitter principle of tar, whence it derives its name (*in pice amarum*). It is present in the heaviest portions of the rectified oil of tar, and when these are treated by potassa, a crystalline compound of the alkali and picamar is formed: this compound, when purified by repeated solution in water and crystallization, is decomposed by phosphoric acid, and the picamar separated by distillation.

Picamar is an oily colourless liquid, of a peculiar odour and very bitter taste. Its sp. gr. is 1.100, and it boils at 545°, being considerably less volatile than creosote. It is insoluble in eupione and sparingly soluble in water; but it dissolves without limit in alcohol and ether. It has no action on test-paper; but it unites with potassa as above mentioned, and strong sulphuric acid dissolves it without decomposition. From its permanence in the air, its fixity when heated, and its oily nature, it is well adapted for greasing machinery and protecting it from rust. Its composition is unknown.

Capnomor.—This substance occurs along with creosote, picamar, and pittacal in the heavy oil of tar. On digesting that oil with solution of potassa, the three latter principles are dissolved, and the capnomor collects on the surface, combined with a little eupione. The capnomor is then dissolved by sulphuric acid, in which eupione is insoluble; and from the solution, on being neutralized with carbonate of potassa, capnomor separates, and is purified by distillation. Its name is derived from καπνος *smoke*, and μοῖρα *part*, because it is one of the ingredients of smoke.

Capnomor is a colourless transparent liquid, of a pungent taste and rather pleasant odour, has a sp. gr. of 0.975, and refracts light almost as powerfully as creosote. It boils at 365°. It is insoluble in water and solution of potassa, and is soluble in alcohol, ether, and eupione. It has the property of dissolving caoutchouc, especially when heated, and is the only ingredient of tar which does so: its presence in coal naphtha is the cause of the solvent action of that liquid on caoutchouc. The composition of capnomor has not been ascertained, though doubtless carbon and hydrogen are its principal ingredients.

Pittacal.—When the heavy oil of tar is digested with a solution of baryta, a fine blue colour appears, which is due to pittacal, from *πιττα pitch*, and *καλλος ornament*. The mode of preparing it has not been described. It is a solid of a beautiful blue colour, which admits of being fixed as a dye. It is very permanent, contains nitrogen as one of its elements, and appears to belong to the same class of bodies as indigo.

PIT-COAL.

Brown Coal is characterized by burning with a peculiar bituminous odour, like that of peat. It is sometimes earthy, but the fibrous structure of the wood from which it is derived is generally more or less distinct, and hence this variety is called *bituminous wood*. *Pitch coal* or *jet*, which is employed for forming ear-rings and other trinkets, is intermediate between brown and black coal, but is perhaps more closely allied to the former than the latter.

Brown coal is found at Bovey in Devonshire (Bovey coal), in Iceland, where it is called *surturbrand*, and in several parts of the continent, especially at the Meissner in Hessia, in Saxony, Prussia, and Styria.

Common or Black Coal.—Of the common or black coal there are several varieties, which differ from each other, not only in the quantity of foreign matters, such as sulphuret of iron and earthy substances, which they contain, but also in the proportion of what may be regarded as essential constituents. Thus some kinds of coal consist almost entirely of carbonaceous matters, and, therefore, form little flame in burning; while others, of which cannel coal is an example, yield a large quantity of inflammable gases by heat, and consequently burn with a large flame. Dr. Thomson has arranged the different kinds of coal which are met with in Britain into four subdivisions. (An. of Phil. xiv.) The first is *caking coal*, because its particles are softened by heat and adhere together, forming a compact mass. The coal found at Newcastle, around Manchester, and many other parts of England, is of this kind. The second is termed *splint coal*, from the splintery appearance of its fracture. The *cherry coal* occurs in Staffordshire, and in the neighbourhood of Glasgow. Its structure is slaty, and it is more easily broken than splint coal, which is much harder. It easily takes fire, and is consumed rapidly, burning with a clear yellow flame. The fourth kind is *cannel coal*, which is found of peculiar purity at Wigan in Lancashire. In Scotland it is known by the name of *parrot coal*. From the brilliancy of the light which it emits while burning, it is sometimes used as a substitute for candles, a practice which is said to have led to the name of *cannel* coal. It has a very compact structure, does not soil the fingers when handled, and admits of being polished. Snuff-boxes and other ornaments are made with this coal; and it is peculiarly well fitted for forming coal gas. According to the experiments of Thomson, these varieties of coal are thus constituted:—

	Caking Coal.	Splint Coal.	Cherry Coal.	Cannel Coal.
Carbon	75.28	75.00	74.45	64.72
Hydrogen	4.18	6.25	12.40	21.56
Nitrogen	15.96	6.25	10.22	13.72
Oxygen	4.58	12.50	2.93	0.00
	100.00	100.00	100.00	100.00

Judging from the quantity of oxidized products (water, carbonic acid, and carbonic oxide) which are procured during the distillation of coal, Henry infers that coal contains more oxygen than was found by Thomson. (Elements, 11th Edit. ii. p. 348.) This opinion is supported by the analysis of Ure, who found 26.66 per cent. of oxygen in splint, and 21.9 in cannel coal. When coal is heated to redness in close vessels, a great quantity of volatile matter is dissipated, and a carbonaceous residue, called *coke*, remains in the retort. The volatile substances are coal tar, acetic acid, water, hydrosulphuric acid, and hydrosulphate and carbonate of ammonia, together with the several gases formerly enumerated. The greater part of these substances, even most of the bituminous principles, are real products, that is, are generated during the distillation.

Glance Coal.—Glance coal, or *anthracite*, differs from common coal, which it frequently accompanies, in containing no bituminous substances, and in not yielding inflammable gases by distillation. Its sole combustible ingredient is carbon, and consequently it burns without flame. It commonly occurs in the immediate vicinity of basalt, under circumstances which lead to the suspicion that it is coal from which the volatile ingredients have been expelled by subterranean heat. At the Meissner, in Hessia, it is found between a bed of brown coal and basalt. Kilkenny coal appears to be a variety of glance coal. (Thomson, An. of Phil. vol. xv.)

SECTION V.

SPIRITUOUS AND ETHEREAL SUBSTANCES.

Alcohol.

Alcohol is the intoxicating ingredient of all spirituous and vinous liquors. It does not exist ready formed in plants, but is a product of the vinous fermentation, the theory of which will be stated in a subsequent section.

Common alcohol or spirit of wine is prepared by distilling whisky or some ardent spirit, and the rectified spirit of wine is procured by a second distillation. The former has a specific gravity of about 0.867, and the latter of 0.835 or 0.84. In this state it contains a quantity of water, from which it may be freed by the action of substances which have a strong affinity for that liquid. Thus, when carbonate of potassa heated to 300° is mixed with spirit of wine, the alkali unites with the water, forming a dense solution, which, on standing, separates from the alcohol, so that the latter may be removed by decantation. To the alcohol, thus deprived of part of its water, fresh portions of the dry carbonate are successively added, until it falls through the spirit without being moistened. Other substances, which have a powerful attraction for water, may be substituted for carbonate of potassa. Gay-Lussac recommends the use of pure lime and baryta (An. de Ch. lxxxvi.); and dry alumina may also be employed. A very convenient process is to mix the alcohol with chloride of calcium in powder, or with quicklime, and draw off the stronger portions by distillation. Another process, which has been recommended for depriving alcohol of water, is to put it into the bladder of an ox, and suspend it over a sand-bath. The water gradually passes through the coats of the bladder, while the pure alcohol is retained; but though this method answers well for strengthening weak spirit, its power of purifying strong alcohol is very questionable. (Journal of Science, xviii.) The strongest alcohol which can be procured by any of these processes has a specific gravity of 0.796 at 60° F. This is called *absolute* alcohol, to denote its entire freedom from water.

An elegant and easy process for procuring absolute alcohol has been proposed by Mr. Graham. (Edin. Philos. Trans. 1828.) A large shallow basin is covered to a small depth with quicklime in coarse powder, and a smaller one containing three or four ounces of commercial alcohol is supported just above it. The whole is placed upon the plate of an air-pump, covered by a low receiver, and the air withdrawn until the alcohol evinces signs of ebullition. Of the mingled vapours of water and alcohol which fill the receiver, the former alone is absorbed by the quicklime, while the latter is unaffected. Now it is found that water cannot remain in alcohol, unless covered by an atmosphere of its own vapour; and consequently the water continues to evaporate without interruption, while the evaporation of the alcohol is entirely arrested by the pressure of the vapour of alcohol on its surface. Common alcohol is in this way entirely deprived of water in the course of about five days. The temperature should be preserved as uniform as possible during the process. Sulphuric acid cannot be substituted for quicklime, since both vapours are absorbed by this liquid.

Alcohol is a colourless limpid fluid, of a penetrating odour, and burning taste. It is highly volatile, boiling, when its density is 0.820, at the temperature of 176° F. The sp. gravity of its vapour, according to Gay-Lussac, is 1.613. Like volatile liquids in general, it produces a considerable degree of cold during evaporation. It has hitherto retained its fluidity under every degree of cold to which it has been exposed.

Alcohol is highly inflammable, and burns with a lambent yellowish-blue flame. Its colour varies considerably with the strength of the alcohol, the blue tint predominating when it is strong, and the yellow when it is diluted. Its combustion is not attended with the least degree of smoke, and the sole products are water and carbonic acid. When transmitted through a red-hot tube of porcelain, it is resolved into carburetted hydrogen, carbonic oxide, and water, and the tube is lined with a small quantity of charcoal.

Alcohol unites with water in every proportion. The act of combining is usually attended with diminution of volume, so that a mixture of 50 measures of alcohol and 50 of water occupies less than 100 measures. Owing to this circumstance, the action is accompanied with increase of temperature. Since the density of the mixture increases as the water predominates, the strength of the spirit may be estimated by its sp. gravity. Equal weights of absolute alcohol and water constitute *proof spirit*, the density of which is 0.917; but the proof spirit employed by the colleges for tinctures has a sp. gravity of 0.930, or 0.935.

Of the salifiable bases alcohol can alone dissolve potassa, soda, lithia, ammonia, and the vegetable alkalies. None of the earths or other metallic oxides are dissolved by it. Most of the acids attack it by the aid of heat, giving rise to a class of bodies to which the name of *ether* is applied. All the salts which are either insoluble, or sparingly soluble in water, are insoluble in alcohol. The efflorescent salts are, likewise, for the most part insoluble in this menstruum; but, on the contrary, it is capable of dissolving nearly all the deliquescent salts, except carbonate of potassa. Many of the vegetable principles, such as sugar, manna, camphor, resins, balsams, and the essential oils, are soluble in alcohol.

The solubility of certain substances in alcohol appears owing to the formation of definite compounds, which are soluble in that liquid. This has been proved of the chlorides of calcium, manganese, and zinc, and of the nitrates of lime and magnesia, by Mr. Graham in the essay above cited. It appears from his experiments that all these bodies unite with alcohol in definite proportion, and yield crystalline compounds, which are deliquescent and soluble both in water and alcohol. From their analogy to hydrates, Mr. Graham has applied to them the name of *alcoates*. These are formed by dissolving the substances in absolute alcohol by means of heat, when on cooling a group of crystals more or less irregular is deposited. The salt and alcohol employed for the purpose should be quite anhydrous; for the crystallization is prevented by a very small quantity of water. Estimating the combining proportion of alcohol at 23.24, the alcoate of chloride of calcium is composed of one equivalent of chloride of calcium, and three equivalents and a half of alcohol. Nitrate of magnesia crystallizes with nine equivalents of alcohol; nitrate of lime with two and a half equivalents; protochloride of manganese with three equivalents; and chloride of zinc with half an equivalent of alcohol.

The following statement of the components of alcohol is drawn from an analysis by Saussure (An. de Ch. lxxxix.):—

Carbon	52.17	12.24	2C	or	24.48	4C
Hydrogen	13.04	3	3H		6	6H
Oxygen	34.79	8	O		16	2O
	100.00	23.24	C^2H^3O		46.48	$C^4H^6O^2$.

Chemists are not agreed about the equivalent of alcohol. It is usually considered as 23.24 or 23, an opinion supported by the composition of the alcoates above mentioned; but some circumstances favour the adoption of twice that number, agreeably to the second of the preceding formulæ. Admitting 23.24 as its equivalent, 100 measures of the vapour of alcohol may be viewed as consisting of 100 measures of olefiant gas and 100 of aqueous vapour; since 0.9808 (sp. gr. of olefiant gas)+0.6202 (sp. gr. of aqueous vapour) =1.6009, which closely coincides with the observed sp. gravity of the vapour of alcohol. The formula of alcohol will in this case be $H^2C^2+\dot{H}$; and alcohol is really resolved into olefiant gas and water by the action of galvanism (Ritchie). Adopting 46.48 as the equivalent of alcohol, then it may be viewed as a compound of etherine (page 250) and aqueous vapour, $H^4C^4+2\dot{H}$; or as a hydrate of ether formed of equal volumes of the vapours of ether and water, united without condensation. On both hypotheses, the calculated density of the vapour of alcohol agrees with observation.

Alcohol exists ready formed in wine and spirituous liquors, and may be collected without heat. Mr. Brande (Phil. Trans. 1811 and 1813) procured it from wine by precipitating the acid and extractive colouring matters by subacetate of lead, and then depriving the alcohol of water by dry carbonate of potassa: the pure alcohol may then be measured in a graduated tube. Gay-Lussac obtained alcohol from wine by distilling it *in vacuo* at the temperature of 60° F. He also succeeded in separating the alcohol by the method of Mr. Brande; but he suggests the employment of litharge in fine powder, instead of subacetate of lead, for precipitating the colouring matter. (Mem. d'Arcueil, vol. iii.)

The preceding researches of Mr. Brande led him to examine the quantity of alcohol contained in spirituous and fermented liquors. According to his experiments, brandy, rum, gin, and whisky, contain from 51 to 54 per cent. of alcohol, of specific gravity 0.825. The stronger wines, such as Lissa, Raisin wine, Marsala, Port, Madeira, Sherry, Teneriffe, Constantia, Malaga, Bucellas, Calcavella, and Vidonia, contain from between 18 or 19 to 25 per cent. of alcohol. In Claret, Sauterne, Burgundy, Hock, Champagne, Hermitage, and Gooseberry wine, the quantity is from 12 to 17 per cent. In cider, perry, ale, and porter, the quantity varies from 4 to near 10 per cent. In all spirits, such as brandy or whisky, the alcohol is simply combined with water; whereas in wine it is in combination with mucilaginous, saccharine, and other vegetable principles, a condition which tends to diminish the action of the alcohol upon the system. This may, perhaps, account for the fact that brandy, which contains little more than twice as much real alcohol as good port wine, has an intoxicating power which is considerably more than double.

Ether.

Most of the stronger acids, when heated with alcohol, give rise to the formation of a volatile inflammable liquid called *ether*, the different kinds of which are further distinguished by the name of the acid with which they were prepared. Thus by sulphuric, hydrochloric, and oxalic ether are meant the ethers formed by means of sulphuric, hydrochloric, and oxalic acid. Most of these ethers actually contain the acid, or the elements of the acid, employed in their production, and, therefore, differ essentially from each other; but that which is formed by means of sulphuric and phosphoric acid is a definite compound of carbon, hydrogen, and oxygen, and is altogether free from acid. It is to this compound the generic term *ether* will always be applied.

In the usual process for preparing ether, strong sulphuric acid is gently poured upon an equal weight of rectified spirit of wine contained in a thin glass retort, and after mixing the fluids together by agitation, which occasions a sudden rise of temperature, the mixture is heated as rapidly as possible until ebullition commences. At the beginning of the process nothing but alcohol passes over; but as soon as the liquid boils, ether is generated, and condenses in the recipient, which is purposely kept cool by the application of ice or moist cloths. When a quantity of ether is collected, equal in general to about half of the alcohol employed, white fumes begin to appear in the retort. At this period, the process should be discontinued, or the receiver changed; for although ether does not cease to be generated, its quantity is less considerable, and several other products make their appearance: thus on continuing the operation, sulphurous acid is disengaged, and a yellowish liquid, commonly called *ethereal oil*, or *oil of wine*, passes over into the receiver. If the heat be still continued, a large quantity of olefiant gas is disengaged, and all the phenomena ensue which were mentioned in the description of that compound. (Page 247.)

Ether, thus formed, is always mixed with alcohol, and generally with some sulphurous acid. To separate these impurities the ether should be agitated with a strong solution of potassa, which neutralizes the acid, while the water unites with the alcohol. The ether is then distilled by a very gentle heat, and may be rendered still stronger by distillation from chloride of calcium.

Pure ether is a colourless limpid liquid, of a hot pungent taste, and fragrant odour. Its sp. gr. is 0.700, or 0.632 according to Lovitz; but that of the shops is 0.74, or even greater, owing to the presence of some alcohol and water. Its volatility is very great: under the atmospheric pressure, ether of sp. gr. 0.720 boils at 96° or 98°, and at —40° in a vacuum. Its evaporation, from the rapidity with which it occurs, occasions intense cold, sufficient in a cool atmosphere for freezing mercury. The sp. gr. of its vapour was found by Gay-Lussac to be 2.586. At —46° it is congealed.

Ether combines with alcohol in every proportion, but is very sparingly soluble in water. When agitated with water, the greater part separates on standing, a small quantity being retained, which imparts an ethereal odour to the water. The ether so washed is very free from alcohol, which combines by preference with the water.

Ether is highly inflammable, burning with a yellow flame, and formation of water and carbonic acid. With oxygen gas its vapour forms a mixture, which explodes violently on the approach of flame, or by the electric spark. On being transmitted through a red-hot porcelain tube it undergoes decomposition, and yields the same products as alcohol.

When a coil of platinum wire is heated to redness, and then suspended above the surface of ether contained in an open vessel, the wire instantly begins to glow, and continues in that state until all the ether is consumed. During this slow combustion, pungent acrid fumes are emitted, which, if received in a separate vessel, condense into a colourless liquid possessed of acid properties. Professor Daniell, who prepared a large quantity of it, was at first inclined to regard it as a new acid, which he described under the name of *lampic acid;* but he has since ascertained that its acidity is owing to acetic acid, which is combined with some compound of carbon and hydrogen different both from ether and alcohol. (Journal of Science, vi. and xii.) Alcohol, when similarly burned, likewise yields acetic acid.

If ether is exposed to light in a vessel partially filled, and which is frequently opened, it gradually absorbs oxygen, and a portion of acetic acid is generated. This change was first noticed by M. Planche, and has been confirmed by Gay-Lussac. (An. de Ch. et de Ph. ii. 98 and 213.) M. Henry of Paris attributes its developement to acetic ether, which he believes to be always contained in sulphuric ether.

The solvent properties of ether are less extensive than those of alcohol. It dissolves the essential oils, resins, and most of the fatty principles. Some of the vegetable alkalies are soluble in it, and it dissolves ammonia; but the fixed alkalies are insoluble in ether.

From the analyses of Saussure, and Dumas and Boullay, the composition of pure ether is admitted to be as follows:—

Carbon . .	64.96	24.48	4 eq.	4C
Hydrogen .	13.47	5	5 eq.	5H
Oxygen . .	21.57	8	1 eq.	O
	100.00	37.48	1 eq.	C^4H^5O.

On comparing the composition of ether with that of alcohol, it will be obvious that these compounds may be regarded as hydrates of etherine (page 244):—thus

	Alcohol.		Ether.	
Etherine . .	28.48	H^4C^4	28.48	H^4C^4
Water . . .	18	$2\dot{H}$	9	$\dot{H}$
	46.48	$H^4C^4+2\dot{H}$	37.48	$H^4C^4+\dot{H}$.

Recent discoveries in organic chemistry have induced Berzelius to regard ether as the oxide of a compound inflammable body called *ethule* or *ethyle* (from ether and υλη principle); and his opinion has been ably supported by Liebig (An. de Ch. et de Ph. lv. 113). On this supposition ethule consists of 4 eq. of carbon and 5 eq. of hydrogen, H^5C^4, so that the formula of ether is H^5C^4+O, a constitution analogous to that of camphor. It may be urged against this view that ethule has not been obtained in a separate form, and that the sp. gr. of the vapours of alcohol and ether is exactly such as would be expected from hydrates of etherine; but as a theory it applies at least as well as the former theory. This will appear from the following comparative view, which represents the composition of the principal compounds described in this section, agreeably to both theories. Etherine is expressed symbolically by En, and ethule by El:—

Alcohol . . .	$En+2\dot{H}$ or $En\dot{H}^2$	$\dot{El}+\dot{H}$ or $\dot{El}\dot{H}$.
Ether . . .	$En+\dot{H}$ or $En\dot{H}$	$El+O$ or $\dot{El}$.
Sulpho-vinic acid .	$En\dot{H}^2+2\dddot{S}$	$\dot{El}\dot{H}+2\dddot{S}$.
Ethero-sulphuric acid	$En\dot{H}+2\dddot{S}$	$\dot{El}+2\dddot{S}$.
Ethero-phosphoric acid	$En\dot{H}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$	$\dot{El}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$.
Oil of wine . .	$2En+2\dddot{S}$	
Hydrochloric ether	$En+HCl$	$El+Cl$.
Hydriodic ether .	$En+HI$	$El+I$.
Hydrobromic ether	$En+HBr$	$El+Br$.
Nitrous ether .	$En\dot{H}+\dddot{N}$	$\dot{El}+\dddot{N}$.
Oxalic ether . .	$En\dot{H}+\overline{O}x$	$\dot{El}+\overline{O}x$.

Benzoic ether .	$\mathrm{En}\dot{\mathrm{H}}+\overline{\mathrm{B}}$	$\dot{\mathrm{E}}\mathrm{l}+\overline{\mathrm{B}}$.
Acetic ether . .	$\mathrm{En}\dot{\mathrm{H}}+\overline{\mathrm{A}}$	$\dot{\mathrm{E}}\mathrm{l}+\overline{\mathrm{A}}$.
Tartaric ether .	$\mathrm{En}\dot{\mathrm{H}}+\overline{\mathrm{T}}$	$\dot{\mathrm{E}}\mathrm{l}+\overline{\mathrm{T}}$.
Pyroxylic spirit .	$\dot{\mathrm{E}}\mathrm{n}+\dot{\mathrm{H}}$	$\mathrm{El}+2\mathrm{O}$

Sulpho-vinic Acid.—This acid was first noticed in the year 1800 by M. Dabit, and has since been studied by Sertuerner, Vogel, and Gay-Lussac, and more lately by Serullas, Hennell, Wöhler and Liebig, and Magnus. (An. de Ch. et de Ph. xlvii. 421; Phil. Trans. 1826 and 1828; and Pog. Annalen, xxvii. 367.) It is formed by the action of strong sulphuric acid on alcohol, and plays an essential part in the formation of ether. When the ingredients for forming ether are intermixed, and before heat is applied, nearly half of the acid exists in the state of sulpho-vinic acid, and may be separated from sulphuric acid by neutralizing the mixture with carbonate of baryta, when an insoluble sulphate and a soluble sulpho-vinate of baryta are generated, the latter of which by evaporation may be obtained in crystals. Soluble sulpho-vinates of lime and oxide of lead may be obtained in the same manner; and by decomposing a solution of these salts by carbonate of potassa or soda, a sulpho-vinate of these alkalies is formed.

Sulpho-vinic acid may be procured in solution by exactly decomposing sulpho-vinate of baryta with sulphuric acid; but it has not been obtained in a dry state except when combined with a base. Hennell considers the acid to be a compound of sulphuric acid with olefiant gas or etherine; but the analyses of sulpho-vinate of baryta by Wöhler, Liebig, and Magnus indicate that it consists of sulphuric acid and alcohol. The crystals of this salt consist of

			Probable Formula.
Sulphuric acid . .	80.2	$2\dddot{\mathrm{S}}$	$\dot{\mathrm{B}}\mathrm{a}+(\mathrm{En}\dot{\mathrm{H}}^2+2\dddot{\mathrm{S}})+\dot{\mathrm{H}}$.
Baryta	76.7	$\dot{\mathrm{B}}\mathrm{a}$	
Alcohol	46.48	$\mathrm{En}\dot{\mathrm{H}}^2$	
Water	9	$\dot{\mathrm{H}}$	

On heating the crystals to 122°, one equivalent of water of crystallization is expelled, and the anhydrous sulpho-vinate remains; but on raising the heat, alcohol is evolved, and sulphate of baryta generated. The salt cannot exist as a sulpho-vinate without possessing sufficient water to convert all its etherine into alcohol. Sulpho-vinic acid may be viewed as a bisulphate of alcohol, and sulpho-vinate of baryta as a double sulphate of baryta and alcohol, in which one half of the acid is neutralized by alcohol and the other half by baryta.

Theory of the Formation of Ether.—It was formerly thought, as first suggested by Fourcroy and Vauquelin, that the sole principle concerned in the formation of ether was the attraction of sulphuric acid for water, by which the alcohol was directly converted into ether. It is apparently in this way that certain substances which are very greedy of water, such as the arsenic and fluoboric acids, and the chlorides of tin and arsenic, effect the conversion of alcohol into ether; but it is now obvious that the ordinary process of forming ether by sulphuric acid, is of a more complex nature. It consists of two distinct parts, namely, the formation of sulpho-vinic acid, and the subsequent decomposition of that acid under the joint agency of heat and sulphuric acid. The affinities which determine the formation of sulpho-vinic acid are the attraction of sulphuric acid for water and for alcohol. The anhydrous acid is divided between the water and alcohol in such a manner that

4 eq. protohydrate of sulphuric acid $4(\dot{H}+\dddot{S})$ yield $(En+2\dot{H})+2\dddot{S}$
and 1 eq. of alcohol . . $En+2\dot{H}$ and $2(2\dot{H}+\dddot{S})$.

The actual composition of the hydrated acid varies with the strength of the acid and alcohol which are used; the diagram is only intended to indicate that one-half of the acid yields its water to the other half, and combines with alcohol. Any excess of alcohol remains uncombined in the mixture, or rises in vapour. If the materials are kept cool, no ether is generated; but as soon as, on applying heat, the temperature rises to about 260°, the sulpho-vinic acid is resolved into hydrated sulphuric acid and ether. The sulpho-vinic acid gradually disappears, and all the sulphuric acid returns to its original state of a hydrate, except that it is rather more diluted than at first. The same acid may be employed to convert successive portions of alcohol into ether, until it becomes too dilute to form sulpho-vinic acid. Consistently with the foregoing explanation, Mr. Hennell obtained ether by heating sulpho-vinate of potassa along with strong sulphuric acid. On distilling sulpho-vinate of potassa with sulphuric acid, not concentrated, but diluted with half its weight of water, he procured alcohol instead of ether. Hence it seems that the first effect of heat on sulpho-vinic acid is to expel alcohol, which, if too much water is not present, is converted into ether in the act of separation.

Ethero-sulphuric Acid.—When the vapour of anhydrous sulphuric acid is introduced into absolute alcohol preserved at a low temperature, a yellowish oily liquid is formed, which consists of hydrated sulphuric and ethero-sulphuric acid, the latter consisting of sulphuric acid and ether, in the ratio indicated by the formula $En\dot{H}+2\dddot{S}$. Its production is owing to the water and ether, which constitute alcohol, uniting with separate portions of anhydrous sulphuric acid. On diluting the mixed acids with water, and neutralizing with carbonate of baryta, an insoluble sulphate and soluble ethero-sulphate of baryta are obtained. The latter salt does not crystallize, and is insoluble in alcohol, in which respects it differs from sulpho-vinate of baryta. The ethero-sulphate of baryta, when dried in vacuo along with sulphuric acid, is anhydrous, and consists of one eq. of baryta and one eq. of ethero-sulphuric acid. Its formula is $\dot{Ba}+(En\dot{H}+2\dddot{S})$.

Magnus, who discovered this acid (Pog. Annalen, xxvii. 378), also formed it by the action of anhydrous sulphuric acid on ether; but in this case some oil of wine was generated at the same time, indicating the separation of a portion of ether into etherine and water. He likewise obtained, by partially decomposing ethero-sulphuric acid by heat, another acid of a similar composition, the nature of which is not yet determined.

Ethero-phosphoric Acid.—It has been known for years that ether, identical with that above described, may be formed by heating alcohol with concentrated phosphoric acid; and Pelouze has lately proved that its formation is preceded by the production of an acid similar to the foregoing. (An. de Ch. et de Ph. lii. 37.) Phosphoric acid of a sp. gr. less than 1.2 has no effect on alcohol; and if in a state of great concentration, phosphoric acid decomposes the alcohol entirely, olefiant gas is disengaged, a liquid like oil of wine passes over, and charcoal is set free,—phenomena similar to those produced by an excess of strong sulphuric acid, and referable to the strong affinity of those acids for water. To prepare ethero-phosphoric acid, mix equal weights of absolute alcohol and phosphoric acid in the state of syrup, heat the mixture for a few minutes to 160°, set aside for twenty-four hours, and then dilute with seven parts of water: the solution, neutralized by carbonate of baryta, boiled to expel free alcohol, and filtered, yields on cooling a white ethero-phosphate of baryta in hexagonal laminæ. A solution of this salt exactly decomposed by sulphuric acid, yields ethero-phosphoric acid.

Ethero-phosphoric acid forms soluble salts with soda, potassa, ammonia, baryta, and magnesia, and insoluble ones with lime, and the oxides of lead, mercury, and silver. A moderately dilute solution suffers very partial decomposition when boiled, which explains why phosphoric acid and alcohol yield but a small portion of ether; but if the concentrated acid is boiled, then ether, traces of an oily matter like oil of wine, and olefiant gas are evolved, leaving at length phosphoric acid and charcoal.

Pelouze considered ethero-phosphoric acid as a compound of phosphoric acid and alcohol, analogous to sulpho-vinic acid; but from a subsequent analysis by Liebig, it appears that it is a compound of phosphoric acid and ether (page 556). The ethero-phosphate of baryta in crystals contains twelve eq. of water of crystallization, which may be expelled by heat, leaving one eq. of acid and two eq. of baryta, $2\dot{Ba}+(En\dot{H}+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}})$. If the ether and baryta were regarded as two bases united with phosphoric acid, the resulting salt, $(2\dot{Ba}+En\dot{H})+\overset{\cdot\cdot\cdot\cdot\cdot}{\underline{P}}$, would be analogous in composition to the anhydrous rhombic phosphate of soda (page 452).

Oil of Wine.—In the process above given for preparing ether, the quantity of alcohol perpetually diminishes, and that of free sulphuric acid augments, the temperature of the mixture rises, and at length the same changes ensue as in the preparation of olefiant gas (page 247). The energetic affinity for water exerted by the sulphuric acid decomposes the ether which would otherwise be formed, olefiant gas is evolved, and the oil of wine collects in the receiver in form of a yellowish fluid. It may be obtained in greater quantity by distilling alcohol with an equal measure of sulphuric acid. The oil of wine should be purified from adhering sulphurous acid and ether by washing with water, and be then dried in vacuo along with sulphuric acid and fused potassa. Oil of wine is also formed when sulpho-vinic acid or a sulpho-vinate is distilled, some alcohol and ether being first disengaged.

The oil of wine has an oily consistence, an aromatic odour, and a bitterish pungent taste. Its sp. gr. is 1.133. It is neutral to test paper, is sparingly soluble in water, but more freely in alcohol and ether, from which it may be recovered by evaporation. It is said by Hennell to consist of sulphuric acid, united with twice as much carbon and hydrogen as in sulpho-vinic acid, and may be hence regarded as a *sulphate of etherine*, the formula of which is $En+\dddot{S}$ or $2En+2\dddot{S}$. According to Serullas it also contains half as much water as is associated in ether with etherine, its formula being $(2En+\dot{H})+2\dddot{S}$. When evaporated with an alkali, or simply boiled along with a little water, it is converted into olefiant gas and sulpho-vinic acid.

In the preparation of ether, the last portions of that fluid contain oil of wine in solution. On distilling such ether from lime, the oil of wine is changed into sulpho-vinic acid, which unites with the lime, and another oily matter is left, which is lighter than water and contains no sulphuric acid. The source and nature of this oil have not been determined.

Hydrochloric Ether.—This compound is generated by the action of hydrochloric acid on alcohol, and may be prepared by several processes:—by distilling alcohol previously saturated with hydrochloric acid gas, or mixed with an equal volume of strong hydrochloric acid; by heating a mixture of 5 parts of alcohol, 5 of strong sulphuric acid, and 12 of fused sea-salt in fine powder; or by distilling alcohol with the chlorides of tin, bismuth, antimony, or arsenic. The products are transmitted through tepid water, by which free alcohol and acid are absorbed, and the pure hydrochloric ether is then received in a vessel surrounded by ice or a freezing mixture.

Hydrochloric ether is a colourless liquid, of a penetrating, somewhat alliaceous, ethereal odour, and a strong rather sweet taste. Its sp. gr. at 41° is

0.774, and it is so volatile that it boils at about 54°. It is neutral to test paper. When inflamed, as it issues from a small aperture, it burns with an emerald-green flame without smoke, yielding abundant vapours of hydrochloric acid. The elements of this ether are in such a ratio that it may be viewed either as a hydrochlorate of etherine or a chloride of ethule (page 556).

Hydriodic Ether.—This ether, analogous in composition to the foregoing, is most conveniently generated by distilling at a gentle heat 2½ parts of iodide of phosphorus with 1 part of alcohol of sp. gr. 0.845. The product is washed with water, and then distilled from chloride of calcium. This ether is colourless, and has a strong ethereal odour, has a sp. gr. of 1.9206 at 72°, and boils at 148°.

Hydrobromic Ether.—This ether is analogous to the preceding, and is prepared by introducing into a retort 40 parts of alcohol of sp. gr. 0.84, and 1 of phosphorus, to which is added drop by drop 7 or 8 parts of bromine, and then distilling. By the reaction of the phosphorus and bromine, phosphorous and hydrobromic acids are generated; and the latter in the nascent state unites with etherine. The product should be washed with water, to which a little potassa is added, in order to separate adhering acid and alcohol.

Nitrous Ether.—The three foregoing ethereal fluids may be viewed as compounds of a hydracid with etherine; but the ether now to be described consists of an acid in combination with sulphuric ether. Nitrous ether is prepared by distilling a mixture of concentrated nitric acid with an equal weight of alcohol; but as the reaction is apt to be exceedingly violent, the process should be conducted with extreme care. The safest method is to add the acid to the alcohol by small quantities at a time, allowing the mixture to cool after each addition before more acid is added. The distillation is then conducted at a very gentle temperature, and the ether collected in Woulfe's apparatus. During the process there is a disengagement of nitrogen, protoxide and binoxide of nitrogen, and carbonic acid gases, from which it is apparent that nitric acid is deoxidized at the expense of the alcohol. According to the researches of Dumas and Boullay, its elements are in such proportion that it may be viewed as a compound of 37.48 parts or one eq. of ether, and 38.15 or one eq. of hyponitrous acid (An. de Ch. et de Ph. xxxii. 26.).

The nitrous agrees with sulphuric ether in its leading properties; but it is still more volatile. When recently distilled from quicklime by a gentle heat, it is quite neutral; but it soon becomes acid by keeping. The products of its spontaneous decomposition are alcohol, nitrous acid, and a little acetic acid. A similar change is instantly effected by mixing the ether with water, or distilling it at a high temperature. It is also decomposed by potassa, and, on evaporation, crystals of the nitrite or hyponitrite of that alkali are deposited (Memoires d'Arcueil, i.).

Oxalic Ether.—This ether is generated by the action of oxalic acid on common ether in its nascent state, and is conveniently prepared by distilling 1 part of alcohol, and 1 of binoxalate of potassa, with 2 parts of sulphuric acid. At first alcohol and then ether pass over, and lastly the oxalic ether collects as an oily liquid at the bottom of the recipient. The alcohol which collects is repeatedly returned to the retort and redistilled. The oxalic ether is quickly washed with water, and boiled along with litharge in fine powder until the boiling point of the liquid descends to 362°. Adhering water and alcohol are thus dissipated, and free oxalic acid combines with oxide of lead: the oxalic ether is then decanted and distilled. It is apt to contain a small quantity of oil of wine.

Oxalic ether is a colourless fluid of an oily aspect, of an aromatic alliaceous odour, and a sp. gr. of 1.0929 at 45°. It boils at 362°. It is neutral to test paper when pure, is sparingly soluble in water, and dissolves in every proportion in alcohol. When kept for some time it is decomposed, and oxalic acid separates in crystals; and with alkalies it readily yields alcohol and oxalic acid. According to the analysis of Dumas and Boullay, it is composed of 36.24 parts or one eq. of oxalic acid, and 37.48 parts or one eq. of ether.

When oxalic ether is briskly agitated with an aqueous solution of pure ammonia, a white precipitate is formed, which, after being washed successively with water and alcohol, was found by Liebig to be pure oxamide (page 500). Alcohol is generated at the same time, the interchange of elements being such, that

$$\begin{array}{llcll} \text{1 eq. oxalic ether} & (En+\dot{H})+(2C+3O) & \text{yield} & \text{1 eq. oxamide} & 2C+N+2H+2O \\ \text{and 1 eq. of ammonia} & 3H+N. & & \text{and 1 eq. alcohol} & En+2\dot{H}. \end{array}$$

When oxalic ether is agitated with alcohol saturated with ammonia, no oxamide is formed, and the solution on evaporation yields crystals, which consist of one eq. of oxalic ether and one eq. of oxalate of ammonia. This compound may be viewed as an ether-oxalate of ammonia, ether-oxalic acid consisting of two eq. of oxalic acid and one eq. of ether, a constitution similar to ethero-sulphuric acid. This compound and oxamide are both generated when dry ammoniacal gas is transmitted over oxalic ether.

Acetic Ether.—This compound may be formed by distilling strong acetic acid with an equal weight of alcohol, but it is more readily produced by distilling to dryness 3 parts of acetate of potassa and 3 of alcohol with 2 parts of sulphuric acid. In each case a considerable quantity of free acetic acid and alcohol are commonly present, and hence the product should be repeatedly returned into the retort and redistilled. Fragments of chloride of calcium are then introduced, which gradually combines with free alcohol, forming, if in quantity, a dense stratum, from which the acetic ether may be removed by a syphon. If acetic acid is present, it should be neutralized by potassa, and the acetic ether again distilled.

Acetic ether is a colourless liquid, of an agreeable but burning taste, and a very fragrant odour. Its density is 0.882 at 65°, and it boils at 165°. It is soluble in 7 or 8 times its weight of water at 60°, and in all proportions in alcohol. It may be preserved without change; but if distilled with pure potassa or lime, an acetate is formed, and alcohol passes over. It consists of one eq. of acetic acid and one eq. of ether. Formic acid, like the acetic, forms an ether with alcohol without the aid of any other acid.

Tartaric, Citric, and Malic Ether, &c.—These ethereal fluids may be obtained by distilling their respective acids with sulphuric acid and alcohol, and in composition are analogous to oxalic and acetic ethers. Kinic and benzoic ethers have also been formed, and the former is solid at common temperatures.

Cyanuric Ether.—This ether was formed by Wöhler by mixing the vapours of anhydrous cyanuric acid and alcohol, and collects as a white powder, nearly insoluble in cold alcohol. It is soluble by aid of heat in a mixture of alcohol and ether, and crystallizes in colourless prisms by evaporation. When heated in open vessels, it fuses and then passes off in vapour. In addition to cyanuric acid and ether, it contains the elements of water; so that it is not analogous to the ethers previously described.

Sulphocyanic Ether.—The substance so termed, Liebig discovered by distilling a mixture of 1 part of sulphocyanuret of potassium, 2 of sulphuric acid, and 3 of strong alcohol. He believes it to be a compound of sulphuret of cyanogen and a carburet of hydrogen. (An. de Ch. et de Ph. xli. 202.)

Chloric Ether.—This name is sometimes applied to the compound of olefiant gas and chlorine (page 248), and sometimes to an oily liquid prepared either by distilling a mixture of sulphuric acid, peroxide of manganese, sea-salt, and alcohol, or by directly transmitting chlorine gas into cold alcohol. It is probable, from the mode of preparation, that the liquid obtained from chlorine and alcohol is identical with chloral (page 222).*

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* Besides those mentioned in the text, there is still another variety of chloric ether, formed by the reciprocal action of alcohol and chloride of

Oxidized Ether.—This name has been applied by Dobereiner to a substance obtained by distilling alcohol with sulphuric acid and peroxide of manganese; and a similar compound is formed by placing alcohol in a dish covered with an open jar, and setting just over the surface of the spirit some moist spongy platinum contained in watch-glasses. The substance obtained by the latter process has been termed *acetal* by Liebig (Pog. Ann. xxvii. 605); but the nature and properties of these products have not yet been determined, nor is it certain that they are definite compounds.

Pyroacetic Spirit.—This compound is generated by distilling the salts of acetic acid, and is one of the ingredients of wood tar. It was obtained by Derosne from acetate of copper, and was called by him pyroacetic ether. Mr. Chevenix formed it by distilling the acetates of manganese, zinc, and lead. It is purified from acetic acid and empyreumatic oil, which pass over at the same time, by admixture with a solution of potassa, and redistillation; and it is subsequently rendered anhydrous by distillation from dry carbonate of potassa or chloride of calcium. It has been examined by Macaire and Marcet (An. of Phil. N. S. viii. 69), and its constitution has been determined by Liebig and Dumas (An. de Ch. et de Ph. xlix).

Pyroacetic spirit, when carefully purified from water, acid, and oil, is a colourless limpid liquid, highly volatile and inflammable, of a peculiar penetrating odour different from both alcohol and ether, and has a density of 0.7921 at 64°. It boils at 132°, and the density of its vapour is 2.019. It unites with water, alcohol, ether, and oil of turpentine in every proportion. It may be exposed for months to the air without change, and be distilled from the alkalies without decomposition; but it is entirely decomposed by sulphuric acid without the formation of ether.

When pyroacetic spirit is distilled from a solution of chloride of lime, the chloride of carbon already described is generated (page 220). By the action of chlorine gas hydrochloric acid is formed, together with a peculiar oily fluid, which has a density of 1.331, and of which 100 parts contain 52.6 of chlorine, 28 of carbon, 2.8 of hydrogen, and 16.6 of oxygen. (Liebig.)

According to the analysis of Liebig, which is confirmed by Dumas, pyroacetic spirit is composed of three eq. of carbon, three eq. of hydrogen, and one eq. of oxygen. These quantities are such that one equivalent of acetic acid, $4C+3H+3O$, exactly corresponds to one equivalent of pyroacetic spirit, $3C+3H+O$, and one equivalent of carbonic acid, $C+2O$. Accordingly both Liebig and Dumas have observed that dry acetate of baryta is converted by heat into pyroacetic spirit and carbonate of baryta.

Pyroxylic Spirit.—When wood is heated in close vessels, it yields a large quantity of impure acetic acid (pyroligneous acid), and charcoal of great

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lime. It was discovered by Mr. Samuel Guthrie, of the state of New York, who prepares it by distilling a gallon from a mixture of three pounds of chloride of lime and two gallons of alcohol of sp. gr. 0.844, and rectifying the product by redistillations, first from a great excess of chloride of lime, and afterwards from strong sulphuric acid. About the same time that Guthrie was making his researches in this country, the same ether was discovered by Soubeiran in France, who obtained it from the same materials which had been employed by Guthrie.

This ether, as obtained by Mr. Guthrie's process, is an extremely volatile liquid, of a sweetish, ethereal odour, and hot, aromatic, peculiar taste. It boils at 166°, and has the sp. gr. of 1.486. It is not acted on by the mineral acids, is slightly soluble in water, and soluble in all proportions in alcohol. When sufficiently diluted with water, it forms an aromatic and saccharine liquid, very grateful to the taste, and acting as a diffusible stimulus, applicable to several states of disease. According to Soubeiran, it consists of two eq. of chlorine 70.84, and one eq. of light carburetted hydrogen 8.12=78.96. As this ether does not contain *chloric acid*, I have elsewhere proposed for it the name of *chlorine ether*, as being more appropriate.—*Ed.*

purity remains in the retort. During this process a peculiar spirituous liquid is formed, which was discovered in 1812 by Mr. P. Taylor,[*] and soon afterwards examined by Macaire and Marcet,[†] who proposed for it the name of *pyroxylic spirit*. This liquid is similar to alcohol in several of its properties, and may be substituted for it in spirit-lamps, and frequently as a solvent for chemical compounds; but it differs essentially from alcohol in not yielding ether by the action of sulphuric acid. It has a strong penetrating ethereal odour, with a flavour like the oil of peppermint, and a pungent pepper-like taste. Its sp. gr. at 65° is 0.804, and it boils at 150°. It burns with a blue flame, without residue.

According to Liebig, pyroxylic spirit contains exactly one more equivalent of oxygen than ether (page 556); but Reichenbach has raised a doubt about the existence of pyroxylic spirit as a definite compound, maintaining it to be a mixture of alcohol and pyroacetic spirit.

SECTION VI.

COLOURING MATTERS.

INFINITE diversity exists in the colour of vegetable substances; but the prevailing tints are red, yellow, blue, and green, or mixtures of these colours. Colouring matter rarely or never occurs in an insulated state, but is always attached to some other proximate principle, such as mucilaginous, extractive, farinaceous, or resinous substances, by which some of its properties, and particularly that of solubility, is greatly influenced. Nearly all kinds of vegetable colouring matter are decomposed by the combined agency of the sun's rays and a moist atmosphere; and they are all, without exception, destroyed by chlorine (page 211). Heat, likewise, has a similar effect, even without being very intense; for a temperature between 300° or 400°, aided by moist air, destroys the colouring ingredient. Acids and alkalies commonly change the tint of vegetable colours, entering into combination with them, so as to form new compounds.

Several of the metallic oxides, and especially alumina and the oxides of iron and tin, form with colouring matter insoluble compounds, to which the name of *lakes* is applied. Lakes are commonly obtained by mixing alum or pure chloride of tin with a coloured solution, and then by means of an alkali precipitating the oxide, which unites with the colour at the moment of separation. On this property are founded many of the processes in dyeing and calico-printing. The art of the dyer consists in giving a uniform and permanent colour to cloth. This is sometimes effected merely by immersing the cloth in the coloured solution; whereas in other instances the affinity between the colour and the fibre of the cloth is so slight, that it only receives a stain which is removed by washing with water. In this case some third substance is requisite, which has an affinity both for the cloth and colouring matter, and which, by combining at the same time with each, may cause the dye to be permanent. A substance of this kind was formerly called a *mordant;* but the term *basis*, introduced by the late Mr. Henry of Manchester, is now more generally employed. The most important bases, and indeed the only ones in common use, are alumina, oxide of iron, and oxide of tin. The two former are exhibited in combination either with the sulphuric or acetic acid, and the latter most commonly as the chloride.

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[*] Quarterly Journal, xiv. 436.

[†] An. of Phil. N. S. viii. 69.

Those colouring substances that adhere to the cloth without a basis are called *substantive* colours, and those which require a basis, *adjective* colours.

Various as are the tints observable in dyed stuffs, they may all be produced by the four simple ones, blue, red, yellow, and black; and hence it will be convenient to treat of colouring matters in that order.

Blue Dyes.—Indigo is chiefly obtained from an American and Asiatic plant, the *Indigofera*, several species of which are cultivated for the purpose. It is likewise extracted from the *Nerium tinctorium;* and an inferior sort is prepared from the *Isatis tinctoria* or *woad*, a native of Europe. Two different methods are employed for its extraction. In one, the recent plant, cut a short time before its flowering, is placed in bundles in a steeping vat, where it is kept down with cross bars of wood, and covered to the depth of an inch or two with water. In a short time fermentation sets in, carbonic acid gas is freely disengaged, and a yellow solution is formed. In the course of ten or twelve hours, when its surface begins to look green from the mixture of blue indigo with the yellow solution, it is drawn off into the beating vat, where it is agitated with paddles, until all the colouring matter is oxidized by absorbing oxygen from the atmosphere, and is deposited in the form of blue insoluble indigo. The other method consists in drying the leaves like hay, removing the leaf from its stalk by threshing, and grinding the former into powder, in which state it is preserved for use. The dye is then extracted either by maceration in water at the temperature of the air, and fermentation; or by digestion in water at 150° or 180°, without being fermented. In either case it is beaten with paddles as before. (Ure in Journ. of Science, N. S. vi. 259.) The process of fermentation, by some thought essential, may be dispensed with. According to Mr. Weston, however, the dye, as contained in the plant, is insoluble in cold water; but by exposure to the air it undergoes a change, in which oxygen acts a part, and by which it is rendered soluble in water. (Journ of Science, N. S. v. 296.)

The indigo of commerce, which occurs in cakes of a deep blue colour and earthy aspect, is a mixed substance, containing, in addition to salts of magnesia and lime, the four following ingredients:—1. a glutinous matter; 2. indigo-brown; 3. indigo-red; 4. indigo-blue. (Berzelius in Lehrbuch, iii. 679.)

1. The *gluten* is obtained by digesting finely pulverized indigo in dilute sulphuric acid, neutralizing with chalk; and evaporating the filtered solution to dryness. The gluten is then taken up by alcohol, and on evaporation is left with the appearance of a yellow or yellowish-brown, transparent, shining varnish. Its odour is similar to that of broth, and it contains nitrogen as one of its elements. It differs, however, from common gluten in its free solubility both in alcohol and water.

2. *Indigo-brown* has not been obtained in a perfectly pure state, owing to its tendency to unite both with acids and alkalies. With the former it yields in general sparingly soluble, and with the latter very soluble compounds, which have a deep brown colour. From indigo, freed from gluten by dilute acid, it is separated by a strong solution of potassa aided by gentle heat; and after dilution with water, without which it passes with difficulty through paper, the liquid is filtered. The solution has a green tint, owing to some indigo-blue being dissolved, and with sulphuric acid yields a bulky semi-gelatinous precipitate of a blackish colour. By dissolving it in solution of carbonate of ammonia, evaporating to dryness, and removing the soluble parts by a small quantity of water, the brown matter is freed from indigo-blue and sulphuric acid. It still, however, contains ammonia, and though this alkali may be expelled by means of hydrated lime or baryta, the indigo-brown is still impure, since it retains some lime or baryta in combination. Like indigo-gluten it contains a considerable quantity of nitrogen as one of its elements. The *indigo-green* of Chevreul is probably a mixture of this substance with indigo-blue.

3. *Indigo-red* is obtained by boiling indigo, previously purified by potassa, in successive portions of strong alcohol as long as a red solution is obtained.

The alcoholic solutions are then concentrated by evaporation, during which the indigo-red is deposited as a blackish-brown powder. The concentrated solution, of a deep red colour, yields by evaporation a compound of indigo-red and indigo-brown with alkali, which is soluble in water.

Indigo-red is insoluble in water and alkalies; but it is soluble, though sparingly, in hot alcohol, and rather more freely in ether. It dissolves in strong sulphuric acid, and forms a dark yellow liquid; and with nitric acid it yields a beautiful purple solution, which speedily becomes yellow by decomposition. When heated *in vacuo*, it yields a gray crystalline sublimate, which, when purified by a second sublimation, is obtained in minute transparent needles, shining and white. This substance, in its relation to reagents, resembles indigo-red; and especially by yielding with nitric acid a similar purple-red solution, which subsequently becomes yellow.

4. *Indigo-blue.*—This term is applied to the real colouring matter of indigo, which is left, though not quite pure, after acting on common indigo with dilute acid, potassa, and alcohol. It is conveniently prepared from the greenish-yellow solution, which dyers make by mixing indigo with green vitriol, hydrate of lime, and water; when the indigo is deoxidized by the protoxide of iron, and yields a soluble compound with lime. On pouring this solution into an excess of hydrochloric acid, while freely exposed to the air, oxygen gas is absorbed, and the indigo is obtained in the form of a blue powder. It may also be procured in a state of great purity by sublimation; but this process is one of delicacy, from the circumstance that the subliming and decomposing points of indigo are very near each other; and minute directions have been given by Mr. Crum for conducting it with success. (An. of Phil. N. S. v.) To be sure of obtaining it quite pure by either process, the indigo should first be purified by the action of dilute acid, potassa, and alcohol.

Pure indigo sublimes at 550°, forming a violet vapour with a tint of red, and condensing into long flat acicular crystals, which appear red by reflected, and blue by transmitted light. It has neither taste nor odour, and it is insoluble in water, alkalies, and ether. Boiling alcohol takes up a trace of it, and acquires a blue tint; but it is generally deposited again on standing. Nitric acid produces a change which has already been described (page 522). Concentrated sulphuric acid, especially that of Nordhausen, dissolves it readily, forming an intensely deep blue solution, commonly termed *sulphate of indigo*, which is employed by dyers for giving the *Saxon blue.* The indigo during solution undergoes a change, and in this modified state it has received the name of *cerulin* from Mr. Crum, who regards it as a compound of one equivalent of indigo and four of water. According to Berzelius the solution is of a more complicated nature, and contains the three following substances: 1. *indigo-purple;* 2. sulphate of indigo; 3. hyposulphate of indigo.

Indigo-purple is chiefly formed when indigo is dissolved in English oil of vitriol, and subsides when the solution is diluted with from 30 to 50 times its weight of water. It was first described under the name of *phenecin*, from φοῖνιξ, purple, by Mr. Crum, who considers it a hydrate of indigo with two equivalents of water. Into the dilute solution, after phenecin is separated, Berzelius inserts fragments of carefully washed flannel, until all the colour is withdrawn from the liquid. The dyed flannel, after the adhering acid is entirely removed, is digested in water, with a little carbonate of ammonia, by which means a blue solution is obtained, consisting of ammonia in combination with sulphate and hyposulphate of indigo. The solution is evaporated to dryness at 140°, and to the residue is added alcohol of 0.833, which dissolves only the hyposulphate.

The compounds of indigo with sulphuric and hyposulphuric acid are considered by Berzelius, not as salts in which indigo acts as a base, but as distinct acids of which indigo is an essential ingredient. *Indigo-sulphuric acid*, as sulphate of indigo may, therefore, be called, is prepared by mixing indigo-sulphate of ammonia with acetate of oxide of lead, when indigo-sulphate of that oxide subsides. This salt is suspended in water, and decomposed by hydrosulphuric acid: the sulphuret of lead is collected on a filter; and the filtered solution, at first colourless or nearly so, owing to deoxidation of indigo by hydrosulphuric acid, but which soon becomes blue by the action of the air, is evaporated at a temperature not exceeding 122° F. The acid is left as a dark blue solid, of a sour astringent taste, soluble in water and alcohol, and capable of forming a distinct group of salts with alkalies. *Indigo-hyposulphuric acid* may be prepared by a similar process.

One of the most remarkable characters of indigo-blue is its susceptibility of being deoxidized, and thus returning to the state in which it appears to exist in the plant, and of again recovering its blue tint by subsequent oxidation. The change is effected by various deoxidizing agents, such as hydrosulphuric acid, hydrosulphate of ammonia, hydrated protoxide of iron, or solution of orpiment in potassa. In the deoxidized state it readily unites with alkaline substances, such as potassa or lime, and forms compounds which are very soluble in water. The method by which dyers prepare their blue vat is founded on these properties. A portion of indigo is put into a tub with about three times its weight of green vitriol and an equal quantity of slaked lime, and water is added. The protoxide of iron, precipitated by lime, gradually deoxidizes the indigo, and in the course of a day or two a yellow solution is obtained. When cotton cloth is moistened with this liquid and exposed to the air, it speedily becomes green from the mixture of colours, and then blue; and as the blue indigo is insoluble, and unites chemically with the fibre of the cloth, the dye is permanent.

Deoxidized indigo has been obtained in a separate state by Liebig. A mixture is made with 1.5 parts of indigo, 2 of green vitriol, 2.5 of hydrate of lime, and 50 or 60 of water; and after an interval of 24 hours the yellow solution is carefully drawn off by a syphon, and mixed with dilute hydrochloric acid. A thick white precipitate falls, which remains without change if carefully excluded from oxygen, and may even be exposed to the air when quite dry; but it rapidly becomes blue by exposure to the atmosphere while moist, or by being covered with aerated water. To this substance Liebig has applied the name of *indigogen;* and he has ascertained that, in passing into blue indigo, it absorbs 11.5 per cent. of oxygen. The necessity for perfectly excluding every source of oxygen renders the preparation of indigogen difficult. All the vessels employed in the process should be filled with hydrogen gas, the water be freed from air by boiling, and as a further protection a little sulphate of ammonia is added both to the acid by which the precipitate is made, and to the water with which it is washed.

The composition of indigogen and indigo-blue will be found at page 522.

Red Dyes.—The chief substances which are employed for the red dye are cochineal, lac, archil, madder, Brazil wood, logwood, and safflower, all of which are adjective colours. The cochineal is obtained from an insect which feeds upon the leaves of several species of the *Cactus*, and which is supposed to derive this colouring matter from its food. It is very soluble in water, and is fixed on cloth by means of alumina or oxide of tin. Its natural colour is crimson; but when bitartrate of potassa is added to the solution, it yields a rich scarlet dye. The beautiful pigment called *carmine* is a lake made of cochineal and alumina, or oxide of tin.

The dye called *archil* is obtained from a peculiar kind of lichen, (*Lichen roccella*,) which grows chiefly in the Canary Islands, and is employed by the Dutch in forming the blue pigment called *litmus* or *turnsol.* The colouring ingredient of litmus is a compound of the red colouring matter of the lichen and an alkali; and hence, on the addition of an acid, the colouring matter is set free, and the red tint of the plant is restored. Litmus is not only used as a dye, but is employed by chemists for detecting the presence of a free acid.

The colouring principle of logwood has been procured in a separate state by Chevreul, who has applied to it the name of *hematin.* (An. de Ch. lxxxi.)

It is obtained in crystals by digesting the aqueous extract of logwood in alcohol, and allowing the alcoholic solution to evaporate spontaneously.

Safflower is the dried flowers of the *Carthamus tinctorius*, which is cultivated in Egypt, Spain, and in some parts of the Levant. The pigment called *rouge* is prepared from this dye.

Madder, extensively employed in dyeing the *Turkey red*, is the root of the *Rubia tinctorum*. A red substance, supposed to be the chief colouring principle of the plant, has been obtained in an insulated state by Robiquet and Colin, who have termed it *alizarine*, from *Ali-zari*, the commercial name by which madder is known in the Levant. Their process has received the following modification by Zenneck. Ten parts of madder are digested in four of ether, the solution is evaporated to the consistence of syrup, and then allowed to become dry by spontaneous evaporation. The residue is pulverized, and sublimed by a gentle heat from a watch glass. The sublimate, which is collected by covering the watch glass with a cone of paper, is deposited in the form of yellowish-red, brilliant, diaphanous, acicular crystals, which are soft, flexible, and heavier than water. They soften when heated, and sublime at a temperature between 500 and 600°, causing an aromatic odour. They are nearly insoluble in cold and very sparingly soluble in hot water. They require for solution 210 times their weight of alcohol, and 160 of ether at 60°. According to Zenneck the acidity of alizarine is very decisive, both in its sour taste, and its power of neutralizing alkalies. It consists, in 100 parts, of 18 of carbon, 20 of hydrogen, and 62 of oxygen. (Journal of Science, N. S. v. 198.)

Yellow Dyes.—The chief yellow dyes are quercitron bark, turmeric, wild American hiccory, fustic, and saffron; all of which are adjective colours. Quercitron bark, which is one of the most important of the yellow dyes, was introduced into notice by Dr. Bancroft. With a basis of alumina, the decoction of this bark gives a bright yellow dye. With oxide of tin it communicates a variety of tints, which may be made to vary from a pale lemon colour to deep orange. With oxide of iron it gives a drab colour.

Turmeric is the root of the *Curcuma longa*, a native of the East Indies. Paper stained with a decoction of this substance constitutes the *turmeric* or *curcuma* paper employed by chemists as a test of free alkali, by the action of which it receives a brown stain.

The colouring ingredient of saffron (*Crocus sativus*) is soluble in water and alcohol, has a bright yellow colour, is rendered blue and then lilac by sulphuric acid, and receives a green tint on the addition of nitric acid. From the great diversity of colours which it is capable of assuming under different circumstances, Bouillon Lagrange and Vogel have proposed for it the name *polychroite*. (An. de Ch. lxxx.)

Black Dyes.—The black dye is made of the same ingredients as writing ink, and, therefore, consists essentially of a compound of oxide of iron with gallic acid and tannin. From the addition of logwood and acetate of copper, the black receives a shade of blue.

By the dexterous combination of the four leading colours, blue, red, yellow, and black, all other shades of colour may be procured. Thus green is communicated by forming a blue ground with indigo, and then adding a yellow by means of quercitron bark.

The reader who is desirous of studying the details of dyeing and calico-printing, a subject which does not fall within the plan of this work, may consult Berthollet's *Elemens de l'Art de la Teinture;* the treatise of Dr. Bancroft on Permanent Colours; a paper by Mr. Henry in the third volume of the Manchester Memoirs; and the Essay of Thenard and Roard in the 74th volume of the *Annales de Chimie.*

SECTION VII.

SUBSTANCES WHICH, SO FAR AS IS KNOWN, DO NOT BELONG TO EITHER OF THE PRECEDING SECTIONS.

Vegetable Albumen.—Under this name is distinguished a vegetable principle which has a close resemblance to animal albumen, especially in the characteristic property of being coagulable by heat. This substance was found by Vogel in the bitter almond, and in the sweet almond by Boullay; it appears to be an ingredient of emulsive seeds generally; and it exists in the sap of many plants. Einhof detected it in wheat, rye, barley, peas, and beans. Vegetable albumen is soluble in cold water, but by a boiling temperature it is coagulated, and thus completely deprived of its solubility. It is insoluble in alcohol, and very sparingly soluble in acids. Alkalies dissolve it readily, and it may be precipitated from them by acids; but the albumen falls in combination with a portion of the acid. Ferrocyanate of potassa and corrosive sublimate act upon it as on solutions of animal albumen.

Vegetable albumen contains nitrogen as one of its elements, and is very prone, when kept in the moist state, to undergo the putrefactive fermentation, emitting an offensive odour, with disengagement of ammonia and formation of acetate of ammonia. During a certain period of putrefaction it has the odour of old cheese. (Berzelius.)

Gluten.—In the separation of starch from wheat flour, as already described (page 536), a gray viscid substance remains, fibrous in its texture, and elastic. Beccaria, who first carefully examined its properties, was struck with its analogy to glue, both in its viscidity as well as its tendency to putrefy like animal matter, and gave it the name of *vegetable gluten.* Einhof has since shown that this gluten is a mixed substance, containing gluten and vegetable albumen.

Pure gluten is obtained by washing dough in water until the starch and soluble parts are removed, and treating the residue with boiling alcohol. On mixing the alcoholic solution with water, and distilling off the spirit, the gluten is deposited in large coherent flakes. As thus obtained it has a pale yellow colour, and a peculiar odour, but no taste, adheres tenaciously to the fingers when handled, and has considerable elasticity. It is insoluble in water and ether, but dissolves readily in hot alcohol, apparently without any change of property; but if the alcoholic solution is evaporated to dryness, the gluten is left as a transparent varnish. It swells up and softens with acetic acid, forming a compound which is soluble in water. It unites also with the mineral acids; and these compounds, excepting that with sulphuric acid, dissolve readily in pure water, but are insoluble when there is an excess of acid. It is dissolved by a dilute solution of potassa, apparently without being decomposed; for the gluten, after being thrown down by the mineral acids, retains its viscidity. In this state, however, it is combined with some of the acid. (Berzelius.)

When gluten is kept in a warm moist situation it ferments, and an acid is formed; but in a few days putrefaction ensues, and an offensive odour, like that of putrefying animal matter, is emitted. According to Proust, who made these spontaneous changes a particular object of study, the process is divisible into two distinct periods. In the first, carbonic acid and hydrogen gases are evolved; and in the second, besides acetic and phosphoric acids and ammonia, two new compounds are generated, for which he proposed the names of *caseic acid* and *caseous oxide.* These are the same principles which are generated during the fermentation of the curd of milk, and their real nature will be considered in the section on milk. It is apparent from these circumstances that gluten contains nitrogen as one of its elements, and that it approaches closely to the nature of animal substances. It has hence been called a vegeto-animal principle.

If gluten is dried by a gentle heat, it contracts in volume, becomes hard and brittle, and may in this state be preserved without change. Exposed to a strong heat, it yields, in addition to the usual inflammable gases, a thick fetid oil, and carbonate of ammonia.

Gluten is present in most kinds of grain, such as wheat, barley, rye, oats, peas, and beans; but the first contains it in by far the largest proportion. This is the reason that wheaten bread is more nutritious than that made with other kinds of flour; for of all vegetable substances gluten appears to be the most nutritive. It is to the presence of gluten that wheat flour owes its property of forming a tenacious paste with water. To the same cause is owing the formation of light spongy bread; the carbonic acid which is disengaged during the fermentation of dough, being detained by the viscid gluten, distends the whole mass, and thus produces the *rising* of the dough. From the experiments of Davy, it appears that good wheat flour contains from 19 to 24 per cent. of gluten. The wheat grown in the south of Europe is richer in gluten than that of colder climates.

M. Taddei, an Italian chemist, has given an account of two principles separable from the gluten of Beccaria by means of boiling alcohol. To the substance soluble in alcohol he has applied the name of *gliadine*, γλια, *gluten;* and to the other that of *zymome*, from ζυμὴ, a ferment. (An. of Phil. xv.) For the latter he has discovered a delicate test in the powder of guaiacum, which when rubbed in a mortar with moist zymome, instantly strikes a beautiful blue colour: and the same tint appears, though less rapidly, when it is kneaded with gluten or dough made with good wheat flour. But with bad flour, the gluten of which has suffered spontaneous decomposition, the blue tint is scarcely visible; and accordingly M. Taddei conceives that useful inferences as to the quality of flour may be drawn from the action of guaiacum.

These views have been criticised by Berzelius, who declares that the substances described by Taddei are nothing else than the gluten and vegetable albumen already described; and the habitual accuracy of Berzelius leaves little chance of error in his statement. The blue tint, above alluded to, must have arisen from the action of guaiacum either on vegetable albumen itself, or on some substance by which it is accompanied in wheat. (An. of Phil. iv. 69, or Lehrbuch, iii. 362.)

Yeast.—This substance is always generated during the vinous fermentation of vegetable juices and decoctions, rising to the surface in the form of a frothy, flocculent, somewhat viscid matter, the nature and composition of which are unknown. It is insoluble in water and alcohol, and in a warm, moist atmosphere gradually putrefies, a sufficient proof that nitrogen is one of its elements. Submitted to a moderate heat, it becomes dry and hard, and may in this state be preserved without change. Heated to redness in close vessels, it yields products similar to those procured under the same circumstances from gluten. To this substance, indeed, yeast is supposed by some chemists to be very closely allied.

The most remarkable property of yeast is that of exciting fermentation. By exposure for a few minutes to the heat of boiling water, it loses this property, but after some time again acquires it. Nothing conclusive is known concerning either the nature of these changes, or the mode in which yeast operates in establishing the fermentative process.

Asparagin.—This principle was discovered by Vauquelin and Robiquet in the juice of the asparagus, from which it is deposited in crystals by evaporation. It is also contained in the root of the marsh-mallow and liquorice. Robiquet, who first procured it from the juice of the recent liquorice root, doubted its identity with asparagin, and gave it the name of *agedoite;* but the mistake has been corrected by M. Plisson.

Asparagin crystallizes in the form of a rectangular octohedron, six-sided prism, or right rhombic prism, is inodorous, and has a cool slightly nauseous taste. In ether and pure alcohol it is insoluble, and requires for solution 58 parts of cold water, but is more freely dissolved by the aid of heat. It has neither an acid nor alkaline reaction with test-paper. Plisson has noticed that when boiled for some time with hydrated oxide of lead or magnesia, it is resolved into ammonia, and a new acid, called the *aspartic*. The possibility of such a change is intelligible from the late analysis of asparagin and aspartic acid by Liebig, as subjoined:—(An. de Ch. et de Ph. liii. 416.)

	Anhydrous Asparagin.			Anhydrous Aspartic Acid.		
Carbon	36.74	48.96	8C	42.16	48.96	8C
Hydrogen	5.94	8	8H	4.37	5	5H
Nitrogen	21.27	28.3	2N	12.20	14.15	N
Oxygen	36.05	48	6O	41.27	48	6O
	100.00	133.26	$C^8H^8N^2O^6$	100.00	116.11	$C^8H^5NO^6$.

It is obvious that one eq. of anhydrous asparagin contains one eq. of aspartic acid and one eq. of ammonia. And yet asparagin is not aspartate of ammonia, since acids do not eliminate aspartic acid nor alkalies ammonia with the facility which would be expected on that supposition. The crystals of asparagin lose 12.133 per cent. of water when heated, or consist of 133.26 parts or one eq. of anhydrous asparagin and 18 or two eq. of water. Aspartic acid is prepared by decomposing the aspartate of oxide of lead by hydrosulphuric acid, and evaporating the filtered solution, when the acid is obtained as a colourless powder composed of minute prismatic crystals, which, like asparagin, contain two eq. of water of crystallization. It has little taste, is sparingly soluble in cold water, and still less so in alcohol. Its aqueous solution is not precipitated by the soluble salts of baryta, lime, lead, magnesia, copper, mercury, or silver. The aspartates, when the taste of the base does not interfere, have the taste of the juice of meat. It yields ammonia when decomposed by heat. (An. de Ch. et de Ph. xxxv. 175, and xl. 309.)

Bassorin was first noticed in gum *Bassora* by Vauquelin. It is an ingredient of gum tragacanth (page 538), and probably occurs in other gums. Salep, from the experiments of Caventou, appears to consist almost totally of bassorin.

Bassorin is characterized by forming with cold water a bulky jelly, which is insoluble in that menstruum, as well as in alcohol and ether. Boiling water does not dissolve it except by long-continued ebullition, when the bassorin at length disappears, and is converted into a substance similar to gum-arabic.

Caffein was discovered in coffee by Robiquet in the year 1821, and was soon after obtained from the same source by Pelletier and Caventou, without a knowledge of the discovery of Robiquet. (An. of Phil. N. S. xii.) It is best prepared by making an aqueous decoction of bruised raw coffee, adding subacetate of oxide of lead as long as a precipitate falls, by which means a large quantity of extractive and colouring matter is thrown down, and then precipitating the excess of oxide of lead by hydrosulphuric acid. The caffein, which is left in solution, is ultimately obtained in crystals by evaporation. Pfaff and Liebig recommend that it should be decolorized by digestion with animal charcoal together with some moist hydrated oxide of lead.

Caffein is a white crystalline volatile matter, sparingly soluble in cold water, but very soluble in boiling water and alcohol, and is deposited from these solutions as they cool, in the form of silky filaments like amianthus. Pelletier, contrary to the opinion of Robiquet, at first regarded it as an alkaline base; but he now admits that it does not affect the vegetable blue colours, nor combine with acids. From a late analysis by Pfaff and Liebig, made with a purer specimen than that analyzed by Pelletier and Dumas, caffein is composed of 48.96 parts or eight eq. of carbon, 5 parts or five eq. of hydrogen, 28.3 or two eq. of nitrogen, and 16 or two eq. of oxygen. (An. de

Ch. et de Ph. xlix. 303.) Though it contains more nitrogen than most animal substances, it does not, under any circumstances, undergo the putrefactive fermentation.

In the precipitate caused in a decoction of coffee by acetate of oxide of lead, tannic acid is present, together with another acid supposed to be peculiar to coffee, and termed by Pfaff caffeic acid.

Cathartin.—This name has been applied by Lassaigne and Feneulle to the active principle of senna. (An. de Ch. et de Ph. vol. xvi.) A similar bitter purgative principle, called *Cytisin*, has been prepared from the Cytisus Alpinus.

Fungin.—This name is applied by Braconnot to the fleshy substance of the mushroom, purified by digestion in hot water, to which a little alkali is added. Fungin is nutritious in a high degree, and in composition is very analogous to animal substances. Like flesh it yields nitrogen gas when digested in dilute nitric acid.

Suberin.—This name has been applied by Chevreul to the cellular tissue of the common cork, the outer bark of the cork-oak, (*quercus suber*), after the astringent, oily, resinous, and other soluble matters have been removed by the action of water and alcohol. Suberin differs from all other vegetable principles by yielding the suberic when treated by nitric acid.

Ulmin, discovered by Klaproth, is a substance which exudes spontaneously from the elm, oak, chesnut, and other trees; and according to Berzelius is a constituent of most kinds of bark. It may be prepared by acting upon elm-bark by hot alcohol and cold water, and then digesting the residue in water, which contains an alkaline carbonate in solution. On neutralizing the alkali with an acid, the ulmin is precipitated.

Ulmin is a dark brown, nearly black substance, is insipid and inodorous, and is very sparingly soluble in water and alcohol. It dissolves freely, on the contrary, in the solution of an alkaline carbonate, and is thrown down by an acid. Ulmin is regarded as an acid by M. P. Boullay, who has proposed for it the name of *ulmic* acid. He found that 100 parts of it contain 56.7 of carbon, and 43.3 of oxygen and hydrogen, in the ratio to form water. According to him it is an ingredient of vegetable mould and turf, and contributes much to the growth of plants. The black matter deposited during the decomposition of prussic acid, supposed by Gay-Lussac to be a carburet of nitrogen, is an acid very similar to the ulmic, and to which he has given the name of *azulmic* acid. (An. de Ch. et de Ph. xliii. 273.)

Lupulin is the name applied by Dr. Ives to the active principle of the hop, but which has not yet been obtained in a state of purity.

Inulin is a white powder like starch, which is spontaneously deposited from a decoction of the roots of the *Inula helenium* or *elecampane*. This substance is insoluble in cold, and soluble in hot water, and is deposited from the latter as it cools, a character which distinguishes it from starch. With iodine it forms a greenish-yellow compound of a perishable nature. Its solution is somewhat mucilaginous; but inulin is distinguished from gum by insolubility in cold water, and in not yielding the saccholactic when digested in nitric acid.

Medullin.—This name was applied by John to the pith of the sun-flower, but its existence as an independent principle is somewhat dubious. The term *pollenin* has been given by the same chemist to the pollen of tulips.

Piperin is the name which is applied to a white crystalline substance extracted from black or white pepper. It is tasteless, and is quite free from pungency, the stimulating property of the pepper being found to reside in a fixed oil. (Pelletier, in An. de Ch. et de Ph. vol. xvi.) Dr. A. T. Thomson has extracted it from chamomile flowers.

A process recommended for its preparation by Vogel consists in digesting for two days 16 ounces of black pepper in coarse powder in twice its weight of water, five times in succession; and digesting the insoluble parts, previously well pressed and dried, for three days in 24 ounces of alcohol. The solution is pressed through linen cloth, filtered, and evaporated to the consistence of syrup; and the impure crystals of piperin, deposited by cooling, are freed from adhering resinous matter by ether, and further purified by animal charcoal, re-solution in alcohol, and a second crystallization.

Piperin crystallizes in four-sided prisms, which have commonly a yellow colour, owing to adhering oil or resin. It is insoluble in cold, and sparingly soluble in hot water; but it is very soluble in alcohol, and less so in ether. Acetic acid also dissolves it, and leaves it by evaporation in feathery crystals. It fuses at 212°, and according to Göbel consists of 80.95 parts of carbon, 8.13 of hydrogen, and 10.92 of oxygen.

Olivile.—When the gum of the olive-tree is dissolved in alcohol, and the solution is allowed to evaporate spontaneously, a peculiar substance, apparently different from the other proximate principles hitherto examined, is deposited either in flattened needles or as a brilliant amylaceous powder. To this Pelletier, its discoverer, has given the name of *Olivile.* (An. of Phil. xii.)

Sarcocoll is the concrete juice of the *Penæa sarcocolla*, a plant which grows in the northern parts of Africa. It is imported in the form of small grains of a yellowish or reddish colour like gum-arabic, to which its properties are similar. It has a sweetish taste, dissolves in the mouth like gum, and forms a mucilage with water. It is distinguished from gum, however, by its solubility in alcohol, and by its aqueous solution being precipitated by tannin. Dr. Thomson, who has given a full account of sarcocoll in his System of Chemistry, considers it closely allied to the saccharine matter of liquorice.

Rhubarbarin is the name employed by Pfaff to designate the principle in which the purgative property of the rhubarb resides. M. Nani of Milan regards the active principle of this plant as a vegetable alkali; but he has not given any proof of its alkaline nature. (Journal of Science, xvi. 172.)

Rhéin.—M. Vaudin has applied this name to a substance which he obtained by gently heating rhubarb in powder with eight times its weight of nitric acid of 1.375, evaporating to the consistence of syrup, and diluting with cold water. Rhéin, which is then deposited, is inodorous, has a slightly bitter taste, and an orange colour. It is sparingly soluble in cold water; but it dissolves in alcohol, ether, and hot water, and its solutions are rendered pale yellow by acids, and rose-red by alkalies. It may be extracted from rhubarb by ether, a fact which proves that it exists ready formed in the plant; and its mode of preparation shows that it possesses unusual permanence, powerfully resisting the action of nitric acid.

Rhaponticin.—This substance was obtained by Hornemann from the *Rheum Rhaponticum.* It was obtained in the form of yellow scales, which are tasteless and inodorous, insoluble in cold water and ether, and requires for solution 24 times its weight of boiling water; and only twice its weight of anhydrous alcohol.

Colocyntin.—This name was applied by Vauquelin to a bitter resinous matter extracted from colocynth by the action of alcohol, and left by evaporation as a brittle substance of a golden-yellow colour. It is slightly soluble in water, is freely dissolved by alcohol and alkalies, and possesses the purgative properties of colocynth. (Journal of Science, xviii. 400.)

Berberin.—This is a yellow bitter principle contained in the alcoholic extract of the root of the barberry.

Bryonin.—This is a bitter, rather poisonous principle, obtained first by Vauquelin and afterwards by Brandes from the root of the *Brionia alba.*

Gentianin is the name applied to the bitter principle of the root of the gentian.

Zanthopicrin is a bitter principle obtained from the bark of the *Zanthoxylum caribæum* by Chevallier and Pelletan. It is of sparing solubility in water, insoluble in ether, very soluble in alcohol, from which it crystallizes by evaporation in yellow acicular crystals of a silky lustre.

Cetrarin is the name applied by Herberger to the bitter principle of Iceland moss.

Scillitin is the name applied by Vogel to the bitter medicinal principle of squills (*Scilla maritima*). It is prepared by evaporating the juice expressed from the fresh root of squills to the consistence of an extract, forming a solution of it in alcohol, which is then evaporated to dryness, and the soluble parts taken up by water. The solution contains scillitin associated with tannic acid and saccharine matter: the former is separated by means of subacetate of oxide of lead; and the latter by forming an alcoholic solution of the scillitin and sugar, freed from tannic acid, and adding ether, which throws down the sugar, leaving most of the scillitin in solution. By evaporation the scillitin remains in the form of a white friable mass of a resinous fracture.

Senegin is the name given by Gehlen to the bitter acrid principle contained in the root of the *Polygala Senega.*

Saponin.—This substance is contained in the root of the *Saponaria officinalis*, and is the cause of the lather which that root forms when agitated with water. It is prepared by evaporating to dryness an aqueous solution of the alcoholic extract of the root, or an alcoholic solution of the aqueous extract. Both solvents are requisite, in order to separate the saponin from resinous and gummy matter with which it is associated in the root.

Arthanatin.—This name was applied by Saladin to a colourless crystalline matter, which is extracted by alcohol from the root of the *Cyclamen Europæum.*

Extractive Matter.—This expression, if applied to one determinate principle supposed to be the same in different plants, is quite inapplicable. It is indeed true that most plants yield to water a substance which differs from gum, sugar, or any proximate principle of vegetables, which, therefore, constitutes a part of what is called an *extract* in pharmacy, and which, for want of a more precise term, may be expressed by the name of *extractive*. It must be remembered, however, that this matter is always mixed with other proximate principles, and that there is no proof whatever of its being identical in different plants. The solution of saffron in hot water, said to afford pure extractive matter by evaporation, contains the colouring matter of the plant, together with all the other vegetable principles of saffron, which happen to be soluble in the menstruum employed.

Plumbagin, extracted by Dulong from the root of the *Plumbago Europæa*, is soluble in water, alcohol, and ether, and crystallizes from its solutions in acicular crystals of a yellow colour. Its aqueous solution is made cherry-red by alkalies, subacetate of oxide of lead, and perchloride of iron; but acids restore the yellow tint, and the plumbagin is found unaltered. Its taste is at first sweet, but is subsequently sharp and acrid, extending to the throat. (Journal of Science, N. S. vi. 191.)

Chlorophyle.—This name has been applied by Pelletier and Caventou to the green colouring matter of leaves. It is prepared by bruising green leaves into a pulp with water, pressing out all the liquid, and boiling the pulp in alcohol. The solution is mixed with water, and the spirit driven off by distillation, when the chlorophyle is left floating on the surface of the water. As thus obtained, it appears to be wax stained with the green colour of the leaves; and from some late observations of Macaire Prinsep, the wax may be removed by ether, and the colouring matter left in a pure state. The red autumnal tint of the leaves, according to the same observer, is the effect of an acid generated in the leaf. The green tint may be restored by the action of an alkali.

Amygdalin.—This substance was extracted in 1830 by Robiquet and Boutron-Charlard from the bitter almond. (An. de Ch. et de Ph. xliv. 352.) The almond, reduced to a pulp, is digested with ether in order to separate its fixed oil, after which it is boiled in 3 or 4 successive portions of alcohol, and the alcoholic solution is distilled in a water bath to the consistence of syrup. This residue is then briskly agitated with ether, and set at rest in a tube placed perpendicularly, when three distinct strata are gradually formed: the upper one is nearly pure ether, the lower is viscid and consists of saccharine matter, and the intermediate stratum, white and semi-solid, contains the amygdalin.

Amygdalin, insoluble in water, dissolves freely in hot alcohol, and crystallizes as the solution cools in white needles, which are not volatile, and remain unchanged in the open air. Its taste is sweet followed by a bitter flavour, analogous to that of the bitter almond, the peculiar flavour of which appears owing to amygdalin. This principle has neither acid nor alkaline properties. It contains nitrogen as one of its elements, and emits a strong odour of ammonia when it is boiled in a solution of potassa. Heated with nitric acid it yields benzoic acid. It certainly has a close relation to benzule, but the nature of that connexion has not yet been traced.

Salicin.—This principle was discovered in 1830 in the bark of the willow (Salix helix) by M. Leroux, who announced it, along with attestations of its virtues from Majendie and other medical authorities, as a cure for intermittent fever of sufficient power to become a substitute for quinia; and observations on its preparation and properties have since been made by Braconnot, Pelouze and J. Gay-Lussac, and Peschier. (An. de Ch. et de Ph. xliii. 440, and xliv. 220, 296, and 418.) It exists in several species of the willow, and Braconnot has met with it in the bark of the poplar, especially of the *Populus tremula.* The most approved method of preparation consists in forming an aqueous decoction of the willow bark, adding subacetate of oxide of lead as long as a precipitate falls, in order to remove colouring matter, boiling with chalk to throw down the excess of oxide of lead, and evaporating the solution. The salicin is deposited in crystals, which may be purified by solution in alcohol and digestion with animal charcoal.

Pure salicin is perfectly white, crystallizes in delicate prisms or needles, and has a very bitter taste. In cold water it is sparingly soluble; but it is freely taken up both by water and alcohol at a boiling temperature, and is insoluble in ether. By strong sulphuric acid in the cold it is decomposed, and the acid acquires a purple tint. Heated with sulphuric acid somewhat diluted, or with strong hydrochloric acid, it is converted into a white insoluble matter of the nature of resin. When digested with eight times its weight of nitric acid, salicin yields a large quantity of carbazotic acid.

Salicin has neither acid nor alkaline properties, and according to Pelouze and J. Gay-Lussac consists of carbon, hydrogen, and oxygen, in the ratio of two equivalents of the first element, two equivalents of the second, and one equivalent of the third.

Populin.—A substance, described under this name, was found by Braconnot in the bark of the *Populus tremula* during his search for salicin. It exists still more plentifully in the leaves of the same tree, and is obtained by throwing down the colouring and extractive matter of an aqueous decoction of the leaves by subacetate of lead, as in the process for salicin, and then evaporating to the consistence of thin syrup: the impure crystals are pressed within linen, mixed with a little animal charcoal, and dissolved in 160 times their weight of boiling water. The filtered solution deposites, in cooling, white, silky, acicular crystals of populin.

Populin requires 2000 times its weight of cold, and 70 of boiling water for solution; but it is much more soluble in hot alcohol. Acids act upon it exactly in the same manner as on salicin, showing that these two substances, if essentially distinct, are very analogous in properties and composition.

Meconin.—This principle was discovered separately by M. Couerbe in 1830, and before that period by M. Dublanc; but we are indebted to the former for a knowledge of its composition and properties (An. de Ch. et de Ph. l. 337). At common temperatures it is a white solid, inodorous, and of a rather acrid taste after some time, though tasteless at first. It begins to liquefy at 190°, and is a limpid liquid at 195°, and may be kept fluid till the temperature falls to 167°. At 311° it sublimes, and condenses on cooling into a white matter like fat. It requires 266 parts of cold, and 18.5 of boiling water for solution, and is very soluble in alcohol, ether, and the essential oils. It crystallizes from these solutions in six-sided prisms, two parallel faces of the prism being larger than the rest, and forming a dihedral summit. When a crystal is put into water which is then heated, the crystal becomes softer, then forms a liquid globule like oil at the bottom of the flask, and then, as the water boils, it soon disappears entirely.

Meconin has neither acid nor alkaline properties. The sulphuric and nitric acids and chlorine decompose it, and produce compounds of a characteristic nature. In sulphuric acid diluted with a quarter or half its weight of water it forms in the cold a colourless solution; but on concentrating to a certain point, the solution acquires a deep blue tint: in this state the meconin is wholly decomposed, and on dilution with water a chestnut matter falls, which is soluble in warm strong sulphuric acid, alkalies, alcohol, and ether, reproducing the green solution with the first, and a rose-red with the two last. Digested in nitric acid it yields a yellow solution, which yields by evaporation elongated crystals of the same colour. Chlorine transmitted over fused meconin gives rise to a fused mass of a reddish-yellow colour, consisting principally of chlorine in union with a new acid, which Couerbe has termed *mechloic acid.*

Meconin is a constituent of opium, and is procured in the process for preparing narceia already described (page 528). By ether narceia is purified in that process from narcotina, fat, and meconin; and on treating the ethereal extract with hot water the meconin is separated from narcotina and fat. It should be purified by a second crystallization, a little animal charcoal being added. Some meconin is likewise present in the impure mass of morphia when precipitated by ammonia (page 525), and is taken up by the alcohol used in its purification. Meconin is present in very small quantity in opium, one pound containing about 2¼ grains, so that it is hopeless to search for it except in large manufacturing operations.

According to Couerbe, 100 parts of meconin contain 60.247 of carbon, 4.756 of hydrogen, and 34.997 of oxygen.

Columbin.—This is a bitter crystalline principle, obtained by M. Wittstock from an alcoholic decoction of columbo root: the solution is concentrated to about a third of its volume, and is then left in a warm place, when yellowish-brown crystals are gradually deposited. It is purified in the usual manner by animal charcoal and solution in hot alcohol, from which it is afterwards obtained in colourless prismatic crystals. (Royal Inst. Journal, N. S. i. 630.)

Elatin.—This matter has been described by Mr. Hennell (R. Inst. Journal, N. S. i. 532), and is prepared by forming an alcoholic decoction of elaterium, distilling off most of the alcohol, and setting aside the remainder for spontaneous evaporation. The residual mass consists of a green resin, in which the medical qualities of elaterium appear to reside, and a crystalline matter: the former is readily taken up by sulphuric ether, and the latter left in a nearly pure state. It is deposited in colourless acicular tufts when its solution in hot alcohol is allowed to cool. In water it is nearly insoluble, and is very slightly dissolved by ether. It has neither acid nor alkaline properties, fuses at a heat between 300° and 400°, and has a bitter taste. According to the analysis of Hennell, 46 parts contain 17 of carbon, 11 of hydrogen, and 18 of oxygen. Elaterium contains 40 per cent. of elatin, and 21 per cent. of the green resin, the remainder being ligneous fibre, earthy matter, and starch.

Sinapisin.—A peculiar principle, called *sulpho-sinapisin*, *sinapisin*, or *sinapin*, has been extracted from mustard seed (sinapis alba) by MM. Henry, jun., and Garot, who at first supposed it to be an acid, but have since corrected their mistake (Phil. Mag. and An. ix. 390). They believe it to contain the elements of sulphuret of cyanogen united with a peculiar organic matter from which the volatile oil of mustard may be developed. It is obtained by forming an aqueous decoction of mustard seed, adding subacetate of oxide of lead as long as a precipitate falls, removing the excess of that oxide by hydrosulphuric acid, and concentrating the filtered solution. The first crop of crystals is purified by a second crystallization.

Pure sinapisin is white and inodorous, has a bitter taste, accompanied with a flavour of mustard, is more soluble in hot water or alcohol than when they are cold, and crystallizes in pearly needles or small prisms arranged in tufts. Heated with hydrochloric acid it is decomposed, emitting an odour of hydrocyanic acid; and when distilled with sulphuric or phosphoric acid, sulphocyanic acid is generated. By the fixed alkalies it is also decomposed: evaporated with potassa, the sulphocyanuret of potassium is generated, and a strong odour of the volatile oil of mustard may be perceived. With persalts of iron a solution of sinapisin strikes a deep red colour.

The ultimate elements contained in 100 parts of sinapisin are 50.504 carbon, 7.795 hydrogen, 4.94 nitrogen, 9.657 sulphur, and 27.104 oxygen.

SECTION VIII.

SPONTANEOUS CHANGES OF VEGETABLE MATTER.

Vegetable substances, for reasons already explained in the remarks introductory to the study of organic chemistry, are very liable to spontaneous decomposition. So long, indeed, as they remain in connexion with the living plant by which they were produced, the tendency of their elements to form new combinations is controlled; but as soon as the vital principle is extinct, of whose agency no satisfactory explanation can at present be afforded, they become subject to the unrestrained influence of chemical affinity. To the spontaneous changes which they then experience from the operation of this power. the term *fermentation* is applied.

As might be expected from the difference in the constitution of different vegetable compounds, they are not all equally prone to fermentation; nor is the nature of the change the same in all. Thus alcohol, the oxalic, acetic, and benzoic acids, and probably the vegetable alkalies, may be kept for years without change, and some of them appear unalterable; while others, such as gluten, sugar, starch, and mucilaginous substances, are very liable to decomposition. In like manner, the spontaneous change sometimes terminates in the formation of sugar, at another time in that of alcohol, at a third in that of acetic acid, and at a fourth in the total dissolution of the substance. This has led to the division of the fermentative processes into four distinct kinds, namely, the *saccharine*, *vinous*, *acetous*, and *putrefactive* fermentation.

Saccharine Fermentation.

The only substance known to be subject to the first kind of fermentation is starch. When gelatinous starch, or amidine, is kept in a moist state for a considerable length of time, a change gradually ensues, and a quantity of sugar, equal to about half the weight of the starch employed, is generated. Exposure to the atmosphere is not necessary to this change, but the quantity of sugar is increased by access of air.

The germination of seeds, as exemplified in the malting of barley, is likewise an instance of the saccharine fermentation; but as it differs in some respects from the process above mentioned, being probably modified by the vitality of the germ, it may with greater propriety be discussed in the following section.

The ripening of fruit has also been regarded as an example of the saccharine fermentation, especially since many fruits, of which the pear and apple are examples, if gathered before their maturity, ripen by keeping; and this view is contended for by M. Couverchel as an inference from his experimental inquiry on the maturation of fruits. (An. de Ch. et de Ph. xlvi. 147.) Proust, who examined the unripe grape in its different stages towards maturity, found that the green fruit contains a large quantity of free acid, chiefly the citric, which gradually disappears as the grape ripens, while its place is occupied by sugar. Couverchel examined the grape, peach, apricot, and pear. He found that the acid and mucilaginous matters of the fruit are diminished, while carbonic acid, water, and sugar are generated: these changes he found to be independent of the oxygen of the air, and to occur whether the fruit is on the tree or removed from it: they arise from reaction among the ingredients of the fruit, rendered operative by heat, but independent of vitality. He considers the developement of sugar and disappearance of acid, which occur during the process of ripening, to be a change purely chemical.

Vinous Fermentation.

The conditions which are required for establishing the vinous fermentation are four in number; namely, the presence of sugar, water, yeast, or some ferment, and a certain temperature. The best mode of studying this process, so as to observe the phenomena and determine the nature of the change, is to place five parts of sugar with about twenty of water in a glass flask furnished with a bent tube, the extremity of which opens under an inverted jar full of water or mercury; and after adding a little yeast, to expose the mixture to a temperature of about 60° or 70°. In a short time bubbles of gas begin to collect in the vicinity of the yeast, and the liquid is soon put into brisk motion, in consequence of the formation and disengagement of a large quantity of gaseous matter; the solution becomes turbid, its temperature rises, and froth collects upon its surface. After continuing for a few days, the evolution of gas begins to abate, and at length ceases altogether; the impurities gradually subside, and leave the liquor clear and transparent.

The only appreciable changes which are found to have occurred during the process are the disappearance of the sugar, and the formation of alcohol, which remains in the flask, and of carbonic acid gas, which is collected in the pneumatic apparatus. A small portion of yeast is indeed decomposed; but the quantity is so minute that it may without inconvenience be left out of consideration. The yeast indeed appears to operate only in exciting the fermentation, without further contributing to the products. The atmospheric air, it is obvious, has no share in the phenomena, since it may be altogether excluded without affecting the result. The theory of the process is founded on the fact that the sugar, which disappears, is almost precisely equal to the united weights of the alcohol and carbonic acid; and hence the former is supposed to be resolved into the two latter. The mode in which this change is conceived to take place has been ably explained by Gay-Lussac, an explanation which will easily be understood by comparing the composition of sugar with that of alcohol. The elements of sugar, which consist of carbon, hydrogen, and oxygen, in the ratio of one equivalent of each (page 535), are multiplied by six, in order to equalize the quantity of hydrogen contained in the two compounds. (An. de Ch. xcv. 317.)

	Sugar.		Alcohol.		Carbonic acid.	
Carbon . .	36.72	6 eq.	24.48	4 eq.	12.24	2 eq.
Hydrogen .	6	6 eq.	6	6 eq.		
Oxygen . .	48	6 eq.	16	2 eq.	32	4 eq.
	90.72		46.48	1 eq.	44.24	2 eq.

It hence appears that 90.72 parts of sugar are capable of supplying 46.48

of alcohol and 44.24 of carbonic acid, nearly equal weights, without any other products.

It admits of doubt whether any substance besides sugar is capable of undergoing the vinous fermentation. The only other principle which is supposed to possess this property is starch, and this opinion chiefly rests on the two following facts. First, It is well known that potatoes, which contain but little sugar, yield a large quantity of alcohol by fermentation, during which the starch disappears. And, secondly, M. Clement procured the same quantity of alcohol from equal weights of malted and unmalted barley. (An. de Ch. et de Ph. v. 422.) Nothing conclusive can be inferred, however, from these data; for, from the facility with which starch is converted into sugar, it is probable that the saccharine may precede the vinous fermentation. This view is, indeed, justified by the practice of distillers, who do not ferment with unmalted barley only, but are obliged to mix with it a certain proportion of malt, which appears to act as a ferment to the unmalted grain.

Though a solution of pure sugar is not susceptible of the vinous fermentation without being mixed with yeast, or some such ferment, yet the saccharine juices of plants do not require the addition of that substance; or in other words, they contain some principle which, like yeast, excites the fermentative process. Thus, must or the juice of the grape ferments spontaneously; but Gay-Lussac has observed that these juices cannot begin to ferment unless they are exposed to the air. By heating must to 212°, and then corking it carefully, the juice may be preserved without change; but if it be exposed to the air for a few seconds only, it absorbs oxygen, and fermentation takes place. From this it would appear that the must contains a principle which is convertible into yeast, or at least acquires the characteristic property of that substance, by absorbing oxygen.

It appears from the experiments of M. Colin, that various substances are capable of acting as a ferment. This property is possessed by gluten and vegetable albumen, caseous matter, albumen, fibrin, gelatin, blood, and urine. In general they act most efficaciously after the commencement of putrefaction; and indeed exposure to oxygen gas seems equally necessary for enabling these substances to act as ferments, as to the principle contained in the juice of fruit.

The various kinds of stimulating fluids, prepared by means of the vinous fermentation, are divisible into wines which are formed from the juices of saccharine fruits, and the various kinds of ale and beer produced from a decoction of the nutritive grains previously malted.

The juice of the grape is superior, for the purpose of making wine, to that of all other fruits, not merely in containing a larger portion of saccharine matter, since this deficiency may be supplied artificially, but in the nature of its acid. The chief or only acidulous principle of the mature grape, ripened in a warm climate, such as Spain, Portugal, or Madeira, is bitartrate of potassa. As this salt is insoluble in alcohol, the greater part of it is deposited during the vinous fermentation; and an additional quantity subsides, constituting the *crust*, during the progress of wine towards its point of highest perfection. The juices of other fruits, on the contrary, such as the gooseberry or currant, contain malic and citric acids, which are soluble both in water and alcohol, and of which therefore they can never be deprived. Consequently these wines are only rendered palatable by the presence of free sugar, which conceals the taste of the acid: and hence it is necessary to arrest the progress of fermentation long before the whole of the saccharine matter is consumed. For the same reason, these wines, unless made very sweet, do not admit of being long kept; for as soon as the free sugar is converted into alcohol by the slow fermentative process, which may be retarded by the addition of brandy, but cannot be prevented, the wine acquires a strong sour taste.

Ale and beer differ from wine in containing a large quantity of mucilaginous and extractive matters derived from the malt with which they are made. From the presence of these substances they always contain a free acid, and are greatly disposed to pass into the acetous fermentation. The sour taste is concealed partly by free sugar, and partly by the bitter flavour of the hop, the presence of which diminishes the tendency to the formation of an acid.

The fermentative process which takes place in dough mixed with yeast, and on which depends the formation of good bread, has been supposed to be of a peculiar kind, and is sometimes designated by the name of *panary fermentation.* The ingenious researches of Dr. Colquhoun, however, leave no doubt that the phenomena are to be ascribed to the saccharine matter of the flour undergoing the vinous fermentation, by which it is resolved into alcohol and carbonic acid. (Brewster's Journal, vi.) Mr. Graham first procured alcohol by distillation from fermented dough, and a Company was formed in London for collecting the spirit emitted by dough in the process of baking.

Acetous Fermentation.

When any liquid which has undergone the vinous fermentation, or even pure alcohol diluted with water, is mixed with yeast, and exposed in a warm place to the open air, an intestine movement speedily commences, heat is developed, the fluid becomes turbid from the deposition of a peculiar filamentous matter, and in general carbonic acid is disengaged. Oxygen is absorbed from the atmosphere. These changes, after continuing a certain time, cease spontaneously; the liquor becomes clear, and instead of alcohol, it is now found to contain acetic acid. This process is called the *acetous fermentation.*

The vinous may easily be made to terminate in the acetous fermentation; nay, the transition takes place so easily, that in many instances, in which it is important to prevent it, this is with difficulty effected. It is the uniform result, if the fermenting liquid be exposed to a warm temperature and to the open air; and the means by which it is avoided is by excluding the atmosphere, or by exposure to cold.

For the acetous fermentation a certain degree of warmth is indispensable. It takes place tardily below 60° F.; at 50° it is very sluggish; and at 32°, or not quite so low, it is wholly arrested. It proceeds with vigour, on the contrary, when the thermometer ranges between 60° and 80°, and is even promoted by a temperature somewhat higher. The presence of water is likewise essential; and a portion of yeast, or some analogous substance, by which the process may be established, must also be present.

The information contained in chemical works relative to the substances susceptible of the acetous fermentation is somewhat confused, a circumstance which appears to have arisen from phenomena of a totally different nature being included under the same name. It seems necessary to distinguish between the mere formation of acetic acid, and the acetous fermentation. Several or perhaps most vegetable substances yield acetic acid when they undergo spontaneous decomposition. Mucilaginous substances in particular, though excluded from the air, gradually become sour; and consistently with this fact, inferior kinds of ale and beer are known to acquire acidity in a short time, even when confined in well-corked bottles. In like manner, a solution of sugar, mixed with water, in which the gluten of wheat has fermented, and kept in close vessels, was found by Fourcroy and Vauquelin to yield acetic acid. All these processes, however, appear essentially different from the proper acetous fermentation above described, being unattended with visible movement in the liquid, with absorption of oxygen, or disengagement of carbonic acid.

The acetous fermentation, in this limited sense, consists in the conversion of alcohol into acetic acid. That this change does really take place is inferred, not only from the disappearance of alcohol and the simultaneous production of acetic acid, but also from the quantity of the latter being precisely proportional to that of the former. The nature of the chemical action requires to be elucidated by future researches. The production of carbonic acid was long considered an essential part of the change: but as it is now known that the acetification of pure alcohol may occur without the formation of carbonic acid, it is probable that the appearance of that gas during the acetous fermentation of vinous liquors is referable to the simultaneous evolution of alcohol from sugar contained in the solution. Looking to the composition of alcohol and acetic acid, and to the fact that alcohol may be acetified by atmospheric oxygen without any carbonic acid being formed, the most feasible theory is, that a certain portion of alcohol and oxygen are resolved into water and acetic acid, the proportions being such that

1 eq. of alcohol	$4C+6H+2O$	yield	1 eq. of acetic acid	$4C+3H+3O$
and 4 eq. of oxygen . .	$4O$		and 3 eq. of water	$3(H+O)$.

This requires, however, a more direct experimental proof than it has hitherto received.

The acetous fermentation is conducted on a large scale for yielding the common vinegar of commerce. In France it is prepared by exposing weak wines to the air during warm weather; and in this country it is made from a solution of brown sugar or molasses, or an infusion of malt. The vinegar thus obtained always contains a large quantity of mucilaginous and other vegetable matters, the presence of which renders it liable to several ulterior changes.

Putrefactive Fermentation.

By this term is implied a process which is not attended with the phenomena of the saccharine, vinous, or acetous fermentation, but during which the vegetable matter is completely decomposed. All proximate principles are not equally liable to this kind of dissolution. Those in which charcoal and hydrogen prevail, such as the oils, resins, and alcohol, do not undergo the putrefactive fermentation; nor do acids, which contain a considerable excess of oxygen, manifest a tendency to suffer this change. Those substances alone are disposed to putrefy, the oxygen and hydrogen of which are in proportion to form water; and such, in particular, as contain nitrogen. Among these, however, a singular difference is observable. Caffein evinces no tendency to spontaneous decomposition; while gluten, which certainly must contain a smaller proportional quantity of nitrogen, putrefies with great facility. It is difficult to assign the precise cause of this difference; but it most probably depends partly upon the mode in which the ultimate elements of bodies are arranged, and partly on their cohesive power;—those substances, the texture of which is the most loose and soft, being, *cæteris paribus*, the most liable to spontaneous decomposition.

The conditions which are required for enabling the putrefactive process to take place, are moisture, air, and a certain temperature.

The presence of a certain degree of moisture is absolutely necessary; and hence vegetable substances, which are disposed to putrefy under favourable circumstances, may be preserved for an indefinite period if carefully dried, and protected from humidity. Water acts apparently by softening the texture, and thus counteracting the agency of cohesion; and a part of the effect may also be owing to its affinity for some of the products of putrefaction. It is not likely that this liquid is actually decomposed, since water appears to be a uniform product.

The air cannot be regarded as absolutely necessary, since putrefaction is found to be produced by the concurrence of the two other conditions only; but the process is without doubt materially promoted by free exposure to the atmosphere. Its operation is of course attributable to the oxygen combining with the carbon and hydrogen of the decaying substance.

The temperature most favourable to the putrefactive process is between 60° and 100°. A strong heat is unfavourable, by expelling moisture; and a cold of 32°, at which water congeals, arrests its progress altogether. The mode in which caloric acts is the same as in all similar cases, namely, by tending to separate elements from one another which are already combined.

The products of the putrefactive fermentation may be divided into the solid, liquid, and gaseous. The liquid are chiefly water, together with a little acetic acid, and probably oil. The gaseous products are light carburetted hydrogen, carbonic acid, and, when nitrogen is present, ammonia. Pure hydrogen, and probably nitrogen, are sometimes disengaged. Thus hydrogen and carbonic acid, according to Proust, are evolved from putrefying gluten; and Saussure obtained the same gases from the putrefaction of wood in close vessels. Under ordinary circumstances, however, the chief gaseous product of decaying plants is light carburetted hydrogen, which is generated in great quantity at the bottom of stagnant pools during summer and autumn (page 245). Another elastic principle, supposed to arise from putrefying vegetable remains, is the noxious miasm of marshes. The origin of these miasms, however, is exceedingly obscure. Every attempt to obtain them in an insulated state has hitherto proved abortive; and, therefore, if they are really a distinct species of matter, they must be regarded, like the effluvia of contagious fevers, as of too subtile a nature for being subjected to chemical analysis.

When the decay of leaves or other parts of plants has proceeded so far that all trace of organization is effaced, a dark pulverulent substance remains, consisting of charcoal combined with a little oxygen and hydrogen. This compound is vegetable mould, which, when mixed with a proper quantity of earth, constitutes the soil necessary to the growth of plants. Saussure, in his excellent *Recherches Chimiques sur la Vegetation*, has described vegetable mould as a substance of uniform composition; and on heating it to redness in close vessels, he procured carburetted hydrogen and carbonic acid gases, water holding acetate or carbonate of ammonia in solution, a minute quantity of empyreumatic oil, and a large residue of charcoal mixed with saline and earthy ingredients. On exposing vegetable mould to the action of light, air, and moisture, a chemical change ensues, the effect of which is to render a portion of it soluble in water, and thus applicable to the nutrition and growth of plants.

SECTION IX.

CHEMICAL PHENOMENA OF GERMINATION AND VEGETATION.

Germination.

Germination is the process by which a new plant originates from seed. A seed consists essentially of two parts, the *germ* of the future plant, endowed with a principle of vitality, and the *cotyledons* or *seed-lobes*, both of which are enveloped in a common covering of cuticle. In the germ two parts, the *radicle* and *plumula*, may be distinguished, the former of which is destined to descend into the earth and constitute the root, the latter to rise into the air and form the stem of the plant. The office of the seed-lobes is to afford nourishment to the young plant, until its organization is so far advanced, that it may draw materials for its growth from extraneous sources. For this reason seeds are composed of highly nutritious ingredients. The chief constituent of most of them is starch, in addition to which they frequently contain gluten, gum, vegetable albumen or curd, and sugar.

The conditions necessary to germination are three-fold; namely, moisture, a certain temperature, and the presence of oxygen gas. The necessity of moisture to this process has been proved by extensive observation. It is well known that the concurrence of other conditions cannot enable seeds to germinate provided they are kept quite dry.

A certain degree of warmth is not less essential than moisture. Germination cannot take place at 32°; and a strong heat, such as that of boiling water, prevents it altogether, by depriving the germ of the vital principle. The most favourable temperature ranges from 60° to 80°, the precise degree varying with the nature of the plant, a circumstance that accounts for the difference in the season of the year at which different seeds begin to germinate.

That the presence of air is necessary to germination was demonstrated by several philosophers, such as Ray, Boyle, Muschenbroeck and Boerhaave, before the chemical nature of the atmosphere was discovered; and Scheele, soon after the discovery of oxygen, proved that beans do not germinate without exposure to that gas. Achard afterwards demonstrated the same fact with respect to seeds in general, and his experiments have been fully confirmed by subsequent observers. It has even been shown by Humboldt, that a dilute solution of chlorine, owing to the tendency of that gas to decompose water and set oxygen at liberty, promotes the germination of seeds. These circumstances account for the fact that seeds, when buried deep in the earth, are unable to germinate.

It is remarkable that the influence of light, which is so favourable to all the subsequent stages of vegetation, is injurious to the process of germination. Ingenhousz and Sennebier have proved that a seed germinates more rapidly in the shade than in light, and in diffused daylight quicker than when exposed to the direct solar rays.

From the preceding remarks it is apparent that when a seed is placed an inch or two under the surface of the ground in spring, and is loosely covered with earth, it is in a state every way conducive to germination. The ground is warmed by absorbing the solar rays, and is moistened by occasional showers; the earth at the same time protects the seed from light, but by its porosity gives free access to the air.

The operation of malting barley, in which the grain is made to germinate by exposure to warmth, air, and humidity, affords the best means of studying the phenomena of germination. In preparing malt, the grain passes through four distinct stages, called *steeping*, *couching*, *flooring*, and *kiln-drying*. In the first it is steeped in water for about two days, when it absorbs moisture, softens, and swells considerably. It is then removed to the *couch-frame*, where it is laid in heaps 30 inches in depth for from 26 to 30 hours. In this situation the grain becomes warm and acquires a disposition to germinate; but as the temperature, in such large heaps, would rise very unequally, and germination consequently be rapid in some portions and slow in others, the process of *flooring* is employed. This consists in laying the grain in strata a few inches thick on large airy but shaded floors, where it remains for about 12 or 14 days until germination has advanced to the extent desired by the malster. During this interval the grain is frequently turned, in order that the temperature of the whole mass should be uniform, that each grain should be duly exposed to the air, and that the radicles of contiguous grains should not become entangled with each other. As soon as saccharine matter is freely developed, germination must be arrested; since otherwise, being taken up as nutriment by the young plant, it would speedily disappear. Accordingly, the grain is removed to the kiln, where it is exposed to a temperature gradually rising from 100° to 160°, or rather higher; the object being, first, to dry the grain completely, and then to provide against any recurrence of germination by destroying the vitality of the plant. The most convenient mode of applying the heat is to place the grain on a metallic net-work, through which passes hot air issuing from a fire made with good coke. The process of malting is not conducted during summer, because in hot weather the grain is apt to become mouldy.

The difference between malted and unmalted barley is readily perceived by the taste; but it will be more correctly appreciated by inspecting the result of Proust's comparative analysis of malted and unmalted barley. (An. de Ch. et de Ph. v.)

	In 100 parts of barley.	In 100 parts of malt.
Resin	1	1
Gum	4	15
Sugar	5	15
Gluten	3	1
Starch	32	56
Hordein	55	12

It is hence apparent that, during germination, the hordein is converted into starch, gum, and sugar; so that from an insoluble material, which could not in that state be applied to the uses of the young plant, two soluble and highly nutritive principles result, which by being dissolved in water are readily absorbed by the radicle.

The chemical changes which take place during germination have been ably investigated by Saussure, whose experiments are detailed in the work to which I have already referred. The leading facts which he determined are the following:—that oxygen gas is consumed, that carbonic acid is evolved, and that the volume of the latter is precisely equal to that of the former. Now since carbonic acid gas contains its own volume of oxygen, it follows that this gas must have united exclusively with carbon. It is likewise obvious that the grain must weigh less after than before germination, provided it is brought to the same state of dryness in both instances. Saussure indeed found that the loss is greater than can be accounted for by the carbon of the carbonic acid which is evolved; and hence he concluded that a portion of water, generated at the expense of the grain itself, is dissipated in drying. According to Proust, the diminution in weight is about a third; but Dr. Thomson affirms that in fifty processes, conducted on a large scale under his inspection, the average loss did not exceed one-fifth.

Growth of Plants.

While a plant differs from an animal in exhibiting no signs of perception or voluntary motion, and in possessing no stomach to serve as a receptacle for its food, there exists between them a close analogy both of parts and functions, which, though not discerned at first, becomes striking on a near examination. The stem and branches act as a frame-work or skeleton for the support and protection of the parts necessary to the life of the individual. The root serves the purpose of a stomach by imbibing nutritious juices from the soil, and thus supplying the plant with materials for its growth. The sap or circulating fluid, composed of water holding in solution saline, extractive, mucilaginous, saccharine, and other soluble substances, rises upwards through the wood in a distinct system of tubes called the *common vessels*, which correspond in their office to the lacteals and pulmonary arteries of animals, and are distributed in minute ramifications over the surface of the leaves. In its passage through this organ, which may be termed the lungs of a plant, the sap is fully exposed to the agency of light and air, experiences a change by which it is more completely adapted to the wants of the vegetable economy, and then descends through the inner layer of the bark in another system of tubes called the *proper vessels*, yielding in its course all the juices and principles peculiar to the plant.

The chemical changes which take place during the circulation of the sap are in general of such a complicated nature, and so much under the control of the vital principle, as to elude the sagacity of the chemist. One part of the subject, however, namely, the reciprocal agency of the atmosphere and growing vegetables on each other, falls within the reach of chemical inquiry, and has accordingly been investigated by several philosophers.

For the leading facts relative to what is called the *respiration* of plants, or the chemical changes which the leaves of growing vegetables produce on the atmosphere, we are indebted to Priestley and Ingenhousz, the former of whom discovered that plants absorb carbonic acid from the air under certain circumstances, and emit oxygen in return; and the latter ascertained that this change occurs only during exposure to the direct rays of the sun. When a healthy plant, the roots of which are supplied with proper nourishment, is exposed to the direct solar beams in a given quantity of atmospheric air, the carbonic acid after a certain interval is removed, and an equal volume of oxygen is substituted for it. If a fresh portion of carbonic acid is supplied, the same result will ensue. In like manner, Sennebier and Woodhouse observed, that when the leaves of a plant are immersed in water, and exposed to the rays of the sun, oxygen gas is disengaged. That the evolution of oxygen in this experiment is accompanied with a proportional absorption of carbonic acid, is proved by employing water deprived of carbonic acid by boiling, in which case little or no oxygen is procured.

Such are the changes induced by plants when exposed to sunshine; but in the dark an opposite effect ensues. Carbonic acid gas is not absorbed under these circumstances, nor is oxygen gas evolved; but, on the contrary, oxygen disappears, and carbonic acid gas is evolved. In the dark, therefore, vegetables deteriorate rather than purify the air, producing the same effect as the respiration of animals.

The cause of these opposite effects has been lately discussed by Professor Burnet, who has offered an ingenious explanation, supported by experiments which appear to me satisfactory. (R. Inst. Journ. N. S. i. 83.) He considers that the influence of vegetation on the atmosphere is owing not to *one* but to *two* functions, *digestion* and *respiration:* the latter is believed to proceed at all times as in animals without intermission, and its uniform effect is the production of carbonic acid; while the former takes place only under the influence of light, and gives rise to evolution of oxygen gas, and the abstraction of carbonic acid. A plant, exposed to sunshine, purifies the air, by absorbing carbonic acid from the atmosphere, as well as that emitted by its own respiration, and emits oxygen gas in return. In the dark, digestion is at a stand, and respiration continuing without intermission, carbonic acid accumulates.

From several of the preceding facts, it is supposed that the oxygen emitted by plants while under the influence of light is derived from the carbonic acid which they absorb, and that the carbon of that gas is applied to the purposes of nutrition. Consistently with this view it has been observed that plants do not thrive when kept in an atmosphere of pure oxygen; and it was found by Dr. Percival and Mr. Henry, that the presence of a little carbonic acid is even favourable to their growth. Saussure, who examined this subject minutely, ascertained that plants grow better in an atmosphere which contains about one-twelfth of carbonic acid than in common air, provided they are exposed to sunshine; but if that gas be present in a greater proportion, its influence is prejudicial. In an atmosphere consisting of one-half of its volume of carbonic acid, the plants perished in seven days; and they did not vegetate at all when that gas was in the proportion of two-thirds. In the shade, the presence of carbonic acid is always detrimental. He likewise observed that the presence of oxygen is necessary, in order that a plant should derive benefit from admixture with carbonic acid.

Saussure is of opinion that plants derive a large quantity of their carbon from the carbonic acid of the atmosphere, an opinion which receives great weight from the two following comparative experiments. On causing a plant to vegetate in pure water, supplied with common air and exposed to light, the carbon of the plant increased in quantity; but when supplied with common air in a dark situation, it even lost a portion of the carbon which it had previously possessed.

Light is necessary to the colour of plants. The experiments of Sennebier and Mr. Gough have shown that the green colour of the leaves is not developed, except when they are in a situation to absorb oxygen and give out carbonic acid.

Though the experiments of different philosophers agree as to the influence of vegetation on the air in sunshine and during the night, very different opinions have been expressed both as to the phenomena occasioned by diffused daylight, and concerning the total effect produced by plants on the constitution of the atmosphere. Priestley found that air, vitiated by combustion or the respiration of animals, and left in contact for several days and nights with a sprig of mint, was gradually restored to its original purity; and hence he inferred that the oxygen gas, consumed during these and various other processes, is restored to the mass of the atmosphere by the agency of growing vegetables. This doctrine was confirmed by the researches of Ingenhousz and Saussure, who found that the quantity of oxygen evolved from plants by day exceeds that of carbonic acid emitted during the night; and Davy arrived at the same conclusions as Priestley. But an opposite opinion has been supported by Mr. Ellis, who, from an extensive series of experiments, contrived with much sagacity, inferred that growing plants give out oxygen only in direct sunshine, while at other times they absorb it; that when exposed to the ordinary vicissitudes of sunshine and shade, light and darkness, they form more carbonic acid in the period of a day and night than they destroy; and, consequently, that the general effect of vegetation on the atmosphere is the same as that produced by animals. (Ellis's Researches and Farther Inquiries on Vegetation, &c.)

The recent experiments of Dr. Daubeny appear decisive of this question. He has convinced himself that in fine weather a plant consisting chiefly of leaves and stems, if confined in the same portion of air night and day, and duly supplied with carbonic acid gas during the sunshine, will go on adding to the proportion of oxygen present, so long as it continues healthy, at least up to a certain point, the slight diminution of oxygen and increase of carbonic acid which takes place during the night, bearing no considerable ratio to the degree in which the opposite effect occurs by day. He accounts for the discordance between his own results and those of Mr. Ellis, by his having carefully removed the plants from the experimenting jar immediately they began to suffer from the heat or confinement, and conducted the experiments on a larger and more suitable scale. (Reports of the British Association for 1834, 436.)

Food of Plants.

The chief source from which plants derive the materials for their growth is the soil. However various the composition of the soil, it consists essentially of two parts, so far as its solid constituents are concerned. One is a certain quantity of earthy matters, such as siliceous earth, clay, lime, and sometimes magnesia; and the other is formed from the remains of animal and vegetable substances, which, when mixed with the former, constitute common mould. A mixture of this kind, moistened by rain, affords the proper nourishment of plants. The water, percolating through the mould, dissolves the soluble salts with which it comes in contact, together with the gaseous, extractive, and other matters which are formed during the decomposition of the animal and vegetable remains. In this state it is readily absorbed by the roots, and conveyed as sap to the leaves, where it undergoes a process of assimilation.

But though this is the natural process by which plants obtain the greater part of their nourishment, and without which they do not arrive at perfect maturity, they may live, grow, and even increase in weight, when wholly deprived of nutrition from this source. Thus in the experiment of Saussure, already described, sprigs of peppermint were found to vegetate in distilled water; and it is well known that many plants grow when merely suspended in the air. In the hot-houses of the botanical garden of Edinburgh, for example, there are two plants, species of the fig-tree, the *Ficus australis* and *Ficus elastica*, the latter of which, as Dr. Graham informs me, has been suspended for ten, and the former for nearly sixteen years, during which time they have continued to send out shoots and leaves.

Before scientific men had learned to appreciate the influence of atmospheric air on vegetation, the increase of carbonaceous matter, which occurs in some of these instances, was supposed to be derived from water, an opinion naturally suggested by the important offices performed by this fluid in the vegetable economy. Without water plants speedily wither and die. It gives the soft parts that degree of succulence necessary for the performance of their functions;—it affords two elements, oxygen and hydrogen, which either as water, or under some other form, are contained in all vegetable products;—and, lastly, the roots absorb from the soil those substances only, which are dissolved or suspended in water. So carefully, indeed, has nature provided against the chance of deficient moisture, that the leaves are endowed with a property both of absorbing aqueous vapour directly from the atmosphere, and of lowering their temperature during the night by radiation so as to cause a deposition of dew upon their surface, in consequence of which, during the driest seasons and in the warmest climates, they frequently continue to convey this fluid to the plant, when it can no longer be obtained in sufficient quantity from the soil. But necessary as water is to vegetable life, it cannot yield to plants a principle which it does not possess. The carbonaceous matter which accumulates in plants, under the circumstances above mentioned, may, with every appearance of justice, be referred to the atmosphere; since we know that carbonic acid exists there, and that growing vegetables have the property of taking carbon from that gas.

When plants are incinerated, their ashes are found to contain saline and earthy matters, the elements of which, if not the compounds themselves, are supposed to be derived from the soil. Such at least is the view deducible from the researches of Saussure, and which might have been anticipated by reasoning on chemical principles. The experiments of M. Schrader, however, lead to a different conclusion. He sowed several kinds of grain, such as barley, wheat, rye, and oats, in pure flowers of sulphur, and supplied the shoots as they grew with nothing but air, light, and distilled water. On incinerating the plants, thus treated, they yielded a greater quantity of saline and earthy matters than were originally present in the seeds.

These results, supposing them accurate, may be accounted for in two ways. It may be supposed, in the first place, that the foreign matters were introduced accidentally from extraneous sources, as by fine particles of dust floating in the atmosphere; or, secondly, it may be conceived, that they were derived from the sulphur, air, and water, with which the plants were supplied. If the latter opinion be adopted, we must infer either that the vital principle, which certainly controls chemical affinity in a surprising manner, and directs this power in the production of new compounds from elementary bodies, may likewise convert one element into another; or that some of the substances, supposed by chemists to be simple, such as oxygen and hydrogen, are compounds, not of two, but of a variety of different principles. As these conjectures are without foundation, and are utterly at variance with the facts and principles of the science, I do not hesitate in adopting the more probable opinion, that the experiments of M. Schrader were influenced by some source of error which escaped detection.

ANIMAL CHEMISTRY.

All distinct compounds, which are derived from the bodies of animals, are called *proximate animal principles*. They are distinguished from inorganic matter by the characters stated in the introduction to organic chemistry. The circumstances which serve to distinguish them from vegetable matter are, the presence of nitrogen, their strong tendency to putrefy, and the highly offensive products to which their spontaneous decomposition gives rise. It should be remembered, however, that nitrogen is likewise a constituent of many vegetable substances; though few of these, the vegeto-animal principles excepted (page 568), are prone to suffer the putrefactive fermentation. It is likewise remarkable that some compounds of animal origin, such as cholesterine and the oils, do not contain nitrogen as one of their elements, and are not disposed to putrefy.

The essential constituents of animal compounds are carbon, hydrogen, oxygen, and nitrogen, besides which some of them contain phosphorus, sulphur, iron, and earthy and saline matters in small quantity. Owing to the presence of sulphur and phosphorus, the process of putrefaction, which will be particularly described hereafter, is frequently attended with the disengagement of hydrosulphuric acid and phosphuretted hydrogen gases. When heated in close vessels, they yield water, carbonic oxide, carburetted hydrogen, probably free nitrogen and hydrogen, carbonate and hydrocyanate of ammonia, and a peculiarly fetid thick oil. The carbonaceous matter left in the retort is less easily burned, and is more effectual as a decolorizing agent, than charcoal derived from vegetable matter.

The principle of the method of analyzing animal substances has already been mentioned (page 495).

In describing the proximate animal principles, the number of which is far less considerable than that of vegetable compounds, the arrangement suggested by Gay-Lussac and Thenard in their *Recherches Physico-Chimiques*, and followed by Thenard in his System of Chemistry, has been adopted. The animal compounds are accordingly arranged in three sections. The first contains substances which are neither acid nor oleaginous; the second comprehends the animal acids; and the third includes the animal oils and fats. Several of the principles belonging to the first division, such as fibrin, albumen, gelatin, caseous matter, and urea, were shown by Gay-Lussac and Thenard to have several points of similarity in their composition. They all contain, for example, a large quantity of carbon, and their hydrogen is in such proportion as to convert all their oxygen into water, and their nitrogen into ammonia. No general laws have been established relative to the constitution of the compounds comprised in the other sections.

PROXIMATE ANIMAL SUBSTANCES.

SECTION I.

SUBSTANCES WHICH ARE NEITHER ACID NOR OLEAGINOUS.

Fibrin.

Fibrin enters largely into the composition of the blood, and is the basis of the muscles; it may be regarded, therefore, as one of the most abundant of the animal principles. It is most conveniently procured by stirring recently drawn blood with a stick during its coagulation, and then washing the adhering fibres with water until they are perfectly white. It may also be obtained from lean beef cut into small slices, the soluble parts being removed by digestion in several successive portions of water.

Fibrin is solid, white, insipid, and inodorous. When moist it is somewhat elastic, but on drying, it becomes hard, brittle, and semi-transparent. In a moist warm situation it readily putrefies. It is insoluble in water at common temperatures, and is dissolved in very minute quantity by the continued action of boiling water. Alcohol, of specific gravity 0.81, converts it into a fatty adipocirous matter, which is soluble in alcohol and ether, but is precipitated by water.

The action of acids on fibrin has been particularly described by Berzelius. (Medico-Chir. Trans. iii. 201.) Digested in concentrated acetic acid, fibrin swells and becomes a bulky tremulous jelly, which dissolves completely, with disengagement of a little nitrogen, in a considerable quantity of hot water.

By the action of nitric acid of specific gravity 1.25, aided by heat, on fibrin, a yellow solution is formed with disengagement of a large quantity of nearly pure nitrogen, in which Berzelius could not detect the least trace of binoxide of nitrogen. After digestion for 24 hours, a pale yellow pulverulent substance is deposited, which Fourcroy and Vauquelin described as a new acid under the name of *yellow acid.* According to Berzelius, however, it is a compound of modified fibrin and nitric acid, together with some malic and nitrous acids. It likewise contains some fatty matter, which may be removed by alcohol. The origin of the nitrogen which is disengaged in the beginning of the process is somewhat obscure. From the total absence of binoxide of nitrogen, it is probable that in the early stages very little, if any, of the nitric acid is decomposed, and that the nitrogen gas is solely or chiefly derived from the fibrin.

Dilute hydrochloric acid hardens without dissolving fibrin, and the strong acid decomposes it. The action of sulphuric acid, according to Braconnot, is very peculiar. When fibrin is mixed with its own weight of concentrated sulphuric acid, a perfect solution ensues, without change of colour, or disengagement of sulphurous acid. On diluting with water, boiling for nine hours, and separating the acid by means of chalk, the filtered solution was found to contain a peculiar white matter, to which Braconnot has applied the name of *leucine.* (An. de Ch. et de Ph. xiii.) Digested in strong sulphuric acid, a dark reddish-brown, nearly black, solution is formed, and the fibrin is carbonized and decomposed.

Fibrin is dissolved by pure potassa, and is thrown down when the solution is neutralized. The fibrin thus precipitated, however, is partially changed, since it is no longer soluble in acetic acid. It is soluble likewise in ammonia.

The following is a tabular view of the composition in 100 parts of fibrin, albumen, gelatin, and urea:—

	Carbon.	Hydrog.	Nitrogen.	Oxygen.	
Fibrin . .	53.36	7.02	19.934	19.685	Gay-L. and Thenard.
Albumen	52.883	7.54	15.705	23.872	Ditto.
	50	7.78	15.55	26.67	Prout.
Gelatin . .	47.881	7.914	16.998	27.207	Gay-L. and Thenard.
Urea . . .	19.99	6.66	46.66	26.66	Prout.

Albumen.

Albumen enters largely into the composition both of animal fluids and solids. Dissolved in water it forms an essential constituent of the serum of the blood, the liquor of the serous cavities, and the fluid of dropsy; and in a solid state it is contained in several of the textures of the body, such as the cellular membrane, the skin, glands, and vessels. From this it appears that albumen exists under two forms, liquid and solid.

Liquid albumen is best procured from the white of eggs, which consists almost solely of this principle, united with water and free soda, and mixed with a small quantity of saline matter. In this state it is a thick glairy fluid, insipid, inodorous, and easily miscible with cold water, in a sufficient quantity of which it is completely dissolved. When exposed in thin layers to a current of air it dries, and becomes a solid and transparent substance, which retains its solubility in water, and may be preserved for any length of time without change; but if kept in its fluid condition it readily putrefies. From the free soda which they contain, albuminous liquids have always an alkaline reaction.

Liquid albumen is coagulated by heat, alcohol, and the stronger acids. Undiluted albumen is coagulated by a temperature of 160°, and when diluted with water at 212° F. Water which contains only 1-1000th of its weight of albumen is rendered opaque by boiling. (Bostock.) On this property is founded the method of clarifying by means of albuminous solutions; for the albumen being coagulated by heat, entangles in its substance all the foreign particles which are not actually dissolved, and carries them with it to the surface of the liquid. The character of being coagulated by hot water distinguishes albumen from all other animal fluids.

The acids differ in their action on albumen. The sulphuric, hydrochloric, nitric, and tannic acids coagulate it; and in each case, some of the acid is retained by the albumen. It is precipitated also by metaphosphoric acid, but not by the phosphoric or pyrophosphoric (page 204). The solution of albumen is not precipitated at all by acetic acid. By maceration in dilute nitric acid for a month, it is converted, according to Mr. Hatchett, into a substance soluble in hot water, and possessed of the leading properties of gelatin. Digested in strong sulphuric acid, the coagulum is dissolved, and a dark solution is formed similar to that produced by the same acid on fibrin; but if the heat be applied very cautiously, the liquid assumes a beautiful red colour. This property was discovered some years ago by Dr. Hope, who informs me that the experiment does not always succeed, the result being influenced by very slight causes.

Albumen is precipitated by several reagents, especially by metallic salts. Of these the most delicate as a test is corrosive sublimate, which causes a milkiness when the albumen is diluted with 2000 parts of water. The precipitate, as stated at page 398, is generally considered as a compound of calomel and albumen; but a late analysis by Rose has proved that it consists of oxide of mercury and albumen (Pog. Ann. xxviii. 132). Other metallic solutions, such as the chlorides of tin and iron, subacetate of oxide of lead, and the sulphates of alumina and oxide of copper, also precipitate albumen; the precipitate in every case consists, according to Rose, of a metallic oxide united with albumen. All these precipitates, not excepting that from corrosive sublimate, dissolve in an excess of albumen, and most of them are soluble in an excess of the metallic salt. Ferrocyanuret of potassium is a test for albumen equally delicate as corrosive sublimate, if not more so, provided acetic acid is previously added to neutralize the alkali.

When an albuminous liquid is exposed to the agency of galvanism, pure soda makes its appearance at the negative wire, and the albumen coagulates around that which is in connexion with the positive pole of the battery. Mr. Brande,* who first observed this phenomenon, ascribes it to the separation of free soda, upon which he supposes the solubility of albumen in water to depend; but Lassaigne† attributes it to the decomposition of chloride of sodium and the developement of acid, which coagulates the albumen. However this may be, galvanism is one of the most elegant and delicate tests which we possess of the presence of albumen in animal fluids.

Chemists are not agreed as to the cause of the coagulation of albumen by alcohol and heat. The explanation usually given is that proposed by Dr. Thomson, who ascribes the solubility of albumen to the presence of free soda, and its coagulation to the removal of the alkali. To this hypothesis Dr. Bostock objects, and with justice, that albuminous liquids do not contain a sufficient quantity of free alkali for the purpose (Medico-Chir. Trans. ii. 175). Were I to hazard an opinion on this subject, it would be the following:—that albumen combines directly with water at the moment of being secreted, at a time when its particles are in a state of minute division; but as its affinity for that liquid is very feeble, the compound is decomposed by slight causes, and the albumen thereby rendered quite insoluble. Silicic acid affords an instance of a similar phenomenon. (Page 325.)

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* Philosophical Transactions for 1809. † An. de Ch. et de Ph. vol. xx.

Albumen coagulates without appearing to undergo any change of composition, but it is quite insoluble in water, and is less liable to putrefy than in its liquid state. It is dissolved by alkalies with disengagement of ammonia, and is precipitated from its solution by acids. In the coagulated state it bears a very close resemblance to fibrin, and is with difficulty distinguished from it. Alcohol, ether, acids, and alkalies, according to Berzelius, act upon each in the same manner. He observes, however, that acetic acid and ammonia dissolve fibrin more easily than coagulated albumen. According to Thenard, they are readily distinguished by means of binoxide of hydrogen, from which fibrin causes evolution of oxygen, while albumen has no action upon it.

Gelatin.

Gelatin exists abundantly in many of the solid parts of the body, especially in the skin, cartilages, tendons, membranes, and bones. According to Berzelius, it is not contained in any of the healthy animal fluids; and Dr. Bostock, with respect to the blood, has demonstrated the accuracy of this statement. (Medico-Chir. Trans. vol. i. and ii.)

Gelatin is distinguished from all animal principles by its ready solubility in boiling water, and by the solution forming a bulky, semitransparent, tremulous jelly as it cools. Its tendency to gelatinize is such, that one part of gelatin, dissolved in 100 parts of water, becomes solid in cooling. This jelly is a hydrate of gelatin, and contains so much water, that it readily liquefies when warmed. On expelling the water by a gentle heat, a brittle mass is left, which retains its solubility in hot water, and may be preserved for any length of time without change. Jelly, on the contrary, soon becomes acid by keeping, and then putrefies.

The common gelatin of commerce is the well-known cement called *glue*, which is prepared by boiling cuttings of parchment, or the skins, ears, and hoofs of animals, and evaporating the solution: it may also be prepared from bones. Isinglass, which is the purest variety of gelatin, is prepared from the sounds of fish of the genus *acipenser* especially from the sturgeon. The animal jelly of the confectioners is made from the feet of calves, the tendinous and ligamentous parts of which yield a large quantity of gelatin.

Gelatin is insoluble in alcohol, but is dissolved readily by most of the diluted acids, which form an excellent solvent for it. Mixed with twice its weight of concentrated sulphuric acid, it dissolves without being charred; and on diluting the solution with water, boiling for several hours, separating the acid by means of chalk, and evaporating the filtered liquid, a peculiar saccharine principle is deposited in crystals. This substance has a sweet taste, somewhat like that of the sugar of grapes, is soluble in water, though less so than common sugar, and is insoluble in alcohol. When heated to redness, it yields ammonia as one of the products, a circumstance which shows that it contains nitrogen. Mixed with yeast, its solution does not undergo the vinous fermentation; and it combines directly with nitric acid. It is hence apparent that, though possessed of a sweet taste, it differs entirely from sugar. This substance was discovered by Braconnot. (An. de Ch. et de Ph. vol. xiii.)

Gelatin is dissolved by the liquid alkalies, and the solution is not precipitated by acids.

Gelatin manifests little tendency to unite with metallic oxides. Corrosive sublimate and subacetate of oxide of lead do not occasion any precipitate in a solution of gelatin, and the salts of tin and silver affect it very slightly. The best precipitant for it is tannic acid. By means of an infusion of gall-nuts, Dr. Bostock detected the presence of gelatin when mixed with 5000 times its weight of water; and its quantity may even be estimated approximately by this reagent (page 515). But since other animal substances, as for example albumen, are precipitated by tannic acid, it cannot be relied on as a test of gelatin. The best character for this substance is that of solubility in hot water, and of forming a jelly as it cools.

Urea.

Urea is procured by evaporating fresh urine to the consistence of a syrup, and then gradually adding to it, when quite cold, pure concentrated nitric acid, which should be free from nitrous acid, till the whole becomes a dark-coloured crystallized mass, which is to be repeatedly washed with ice-cold water, and then dried by pressure between folds of bibulous paper. To the nitrate of urea, thus procured, a pretty strong solution of carbonate of potassa is added, until the acid is neutralized; and the solution is afterwards concentrated by evaporation, and set aside, in order that the nitre may separate in crystals. Dr. Prout recommends that the residual liquid, which is an impure solution of urea, should be made up into a thin paste with animal charcoal, and be allowed to remain in that state for a few hours. The paste is then mixed with cold water, which takes up the urea, while the colouring matter is retained by the charcoal; and the colourless solution is evaporated to dryness at a low temperature. The residue is then boiled in pure alcohol, by which the urea is dissolved, and from which it is deposited in crystals on cooling. (Medico-Chir. Trans. viii. 529.) In order to obtain them quite colourless, it is necessary to redissolve in alcohol, and crystallize a second or even a third time.

The crytals of pure urea are transparent and colourless, of a slight pearly lustre, and have commonly the form of a four-sided prism. It leaves a sensation of coldness on the tongue like nitre, and its smell is faint and peculiar, but not urinous. Its specific gravity is about 1.35. It does not affect the colour of litmus or turmeric paper. In a moist atmosphere it deliquesces slightly; but otherwise it undergoes no change on exposure to the air. (Prout.) It is fused at 248°, and at a rather higher temperature it is decomposed, being resolved chiefly into carbonate of ammonia and cyanuric acid, the latter of which, if the heat be not incautiously raised, is left in the retort. (Page 273.)

Water at 60° dissolves more than its own weight of urea, and boiling water takes up an unlimited quantity. It requires for solution about five times its weight of alcohol of specific gravity 0.816 at 60°, and rather less than its own weight at a boiling temperature. The aqueous solution of pure urea may be exposed to the atmosphere for several months, or be heated to the boiling point, without change; but, on the contrary, if the other constituents of urine are present, it putrefies with rapidity, and is decomposed by a temperature of 212°, being almost entirely resolved into carbonate of ammonia by continued ebullition.

The pure fixed alkalies and alkaline earths decompose urea, especially by the aid of heat, carbonate of ammonia being the chief product.

Though urea has not any distinct alkaline properties, it unites with the nitric and oxalic acids, forming sparingly soluble compounds, which crystallize in scales of a pearly lustre. This property affords an excellent test of the presence of urea. Both compounds have an acid reaction, and the nitrate consists of 54.15 parts or one equivalent of nitric acid, and 60.54 parts or one equivalent of urea.

Urea has been carefully analyzed by Dr. Prout, and the accuracy of his analysis is amply attested by the late researches of Liebig and Wöhler. Its equivalent is 60.54; and its elements, as already explained (page 271), are in precisely the same ratio as the hydrated cyanate of ammonia.

A singular instance of the artificial production of urea has been noticed by Wöhler. It is formed by the action of ammonia on cyanogen, as also by direct contact of cyanic acid and ammonia; but the best mode of preparing it is by decomposing cyanate of oxide of silver with hydrochlorate of ammonia, or cyanate of oxide of lead with ammonia, the action being promoted by a gentle heat. In the last case, oxide of lead is set free, and the only other product appears in colourless, transparent, four-sided, rectangular crystals. These crystals, judging by the mode of preparation, must be cyanate of ammonia; but yet no ammonia is evolved from them by the action of potassa: the stronger acids do not, as with other cyanates, cause an evolution of carbonic and cyanic acids; nor do they yield precipitates with salts of lead and silver. In fact, though procured by the mutual action of cyanic acid and ammonia, and containing the very same elements (page 271), the characters above mentioned do not indicate the presence of either; but on the contrary the crystals agree with urea obtained from urine in composition and in all their chemical properties. (Journal of Science, N. S. iii. 491.) The cyanic acid above referred to is that discovered by Wöhler.

Sugar of Milk and Sugar of Diabetes.

Sugar of Milk.—The saccharine principle of milk is obtained from whey by evaporating that liquid to the consistence of syrup, and allowing it to cool. It is afterwards purified by means of albumen and a second crystallization.

The sugar of milk has a sweet taste, though less so than the sugar of the cane, from which it differs essentially in several other respects. Thus it requires seven parts of cold and four of boiling water for solution, and is insoluble in alcohol. It is not susceptible of undergoing the vinous fermentation; and when digested with nitric acid it yields saccholactic acid, a property first noticed by Scheele, and which distinguishes the saccharine principle of milk from every other species of sugar. Like starch, it is convertible into real sugar by being boiled in water acidulated with sulphuric acid.

Sugar of milk contains no nitrogen, and according to the analysis of Gay-Lussac and Thenard, is very analogous to common sugar in the proportion of its elements.

Sugar of Diabetes.—In the disease called *diabetes* the urine contains a peculiar saccharine matter, which, when properly purified, appears identical both in properties and composition with vegetable sugar, approaching nearer to the sugar of grapes than that from the sugar-cane. This kind of sugar is obtained in an irregularly crystalline mass by evaporating diabetic urine to the consistence of syrup, and keeping it in a warm place for several days. It is purified by washing the mass with alcohol, either cold or at most gently heated, till that liquid comes off colourless, and then dissolving it in hot alcohol. By repeated crystallization it is thus rendered quite pure. (Prout.)

A few other principles yet remain to be considered, such as the colouring principle of the blood, caseous matter, and mucus; but these will be more conveniently studied in subsequent sections.

SECTION II.

ANIMAL ACIDS.

In animal bodies several acids are found, such as sulphuric, hydrochloric, phosphoric, acetic, &c., which belong equally to the mineral or vegetable kingdom, and which have consequently been described in other parts of the work. In this section are included those acids only which are believed to be peculiar to animal bodies.

Uric or Lithic Acid.—This acid is a common constituent of urinary and gouty concretions, and is always present in healthy urine, combined with ammonia or some other alkali. The urine of birds of prey, such as the eagle, and of the *boa constrictor* and other serpents, consists almost solely of urate of ammonia, from which pure uric acid may be procured by a very simple process. For this purpose the solid urine of the *boa constrictor* is reduced to a fine powder, and digested in a solution of pure potassa, in which it is readily dissolved with disengagement of ammonia. The urate of potassa is then decomposed by adding acetic, hydrochloric, or sulphuric acid in slight excess, when the uric acid is thrown down, and, after being washed, is collected on a filter. On its first separation from the alkali it is in the form of a gelatinous hydrate, but in a short time this compound is decomposed spontaneously, and the uric acid subsides in small crystals.

Pure uric acid is white, tasteless, and inodorous. It is insoluble in alcohol, and is dissolved very sparingly by cold or hot water, requiring about 10,000 times its weight of that fluid at 60° F. for solution. (Prout.) It reddens litmus paper, and unites with alkalies, forming salts which are called *urates* or *lithates*. The uric acid does not effervesce with alkaline carbonates; but Dr. Thomson affirms that when boiled for some time with carbonate of soda, the whole of the carbonic acid is expelled. A current of carbonic acid, on the contrary, throws down the uric acid when dissolved by potassa. This acid undergoes no change by exposure to the air.

Of the acids none exert any peculiar action on the uric excepting nitric acid. When a few drops of nitric acid, slightly diluted, are mixed on a watch-glass with uric acid, and the liquid is evaporated to dryness, a beautiful purple colour comes into view, the tint of which is improved by the addition of water. This character affords an unequivocal test of the presence of uric acid. The nature of the change will be considered immediately.

Uric acid is decomposed by chlorine. Liebig has observed, that when dry uric acid is heated with dry chlorine, an enormous quantity of cyanic and muriatic acid is generated. If the uric acid is moist, chlorine then gives rise to the disengagement of carbonic and cyanic acids; while in solution there remain hydrochloric acid, ammonia, and much oxalic acid.

According to a late analysis by Liebig, uric acid is thus constituted:—(An. de Ch. et de Ph. lv. 58.)

Carbon	36.11	30.6	or	5 eq.
Hydrogen	2.34	2		2 eq.
Nitrogen	33.36	28.3		2 eq.
Oxygen	28.19	24		3 eq.
	100.00	84.9		1 eq.

Liebig has given strong evidence to prove that the foregoing constitution is more correct than that of Prout, who found six eq. of carbon instead of five. Crystallized uric acid is considered by most chemists to be anhydrous; but Dr. Thomson maintains that at 400° it loses precisely two equivalents of water.

The salts of uric acid have been described by Henry (Manchester Memoirs, vol. ii. N. S.) The principal ones yet examined are the urates of ammonia, potassa, and soda. Urate of ammonia is soluble to a considerable extent in boiling, but more sparingly in cold water. The urates of soda and potassa, if neutral, are of very sparing solubility; but an excess of either alkali takes up a large quantity of the acid. The former was found by Wollaston to be the chief constituent of gouty concretions.

When uric acid is heated in a retort, carbonate and hydrocyanate of ammonia are generated, and a volatile acid sublimes, called *pyro-uric acid*, which was formerly described by Henry, and has since been studied by Chevallier and Lassaigne, Liebig, and Wöhler. The two latter chemists have noticed, that pyro-uric is identical with cyanuric acid (page 273); and Wöhler finds that urea, as well as cyanuric acid, is an essential product of the destructive distillation of uric acid.

Purpuric Acid.—This compound was first recognized as a distinct acid by Prout, and was described by him in the Philosophical Transactions for 1818. Though colourless itself, it has a remarkable tendency to form red or purple-coloured salts with alkaline bases, a character by which it is distinguished from all other substances, and to which it owes the name of *purpuric acid*, suggested by Wollaston. Thus the purple residue above mentioned, as indicative of the presence of uric acid, is purpurate of ammonia, which is always generated when the uric is decomposed by nitric acid.

Purpuric acid may be prepared by the following process, for the outline of which I am indebted to directions kindly given me by Prout. Let 200 grains of uric acid, prepared from the urine of the *boa constrictor*, be dissolved in 300 grains of pure nitric acid diluted with an equal weight of water, the uric acid being added gradually in order that the heat may not be excessive. Effervescence ensues after each addition, nitrous acid fumes appear, heat is evolved, and a colourless solution is formed, which, on standing in a cool place for some hours, yields colourless crystals, which have the outline of an oblique rhomboidal prism. By gentle evaporation an additional quantity may be obtained. They contain nitric and purpuric acid and ammonia, should be dissolved in water, and be exactly neutralized by pure ammonia; and the liquid is then digested in a solution of potassa, until the ammonia is wholly expelled. On pouring this solution into dilute sulphuric acid, purpuric acid is set free, which, being insoluble in water, subsides as a granular powder, of a white colour if pure, but commonly of a yellowish-white tint.

Considerable uncertainty prevails as to the nature of purpuric acid. Vauquelin denied that its salts have a purple colour, attributing that tint to some impurity, and Lassaigne is inclined to the same opinion (An. de Ch. et de Ph. xxii. 334); but from the intense colour given even by a very minute quantity of purpuric acid, the opinion of Dr. Prout appears to me the more probable. The composition of the acid is, likewise, unsettled; for Prout has expressed a doubt of the accuracy of the analysis which he formerly published.

The name of *erythric acid* (from *ερυθραίνειν, to redden*) was applied by Brugnatelli to a substance which he procured by the action of nitric on uric acid. It obviously contains purpuric acid, and Prout thinks it probable that it is a supersalt, consisting of purpuric and nitric acids, and ammonia, being probably identical with the crystals above mentioned.

Rosacic Acid.—This name was applied by Proust to a peculiar acid supposed to exist in the red matter, commonly called by medical practitioners the *lateritious sediment*, which is deposited from the urine in some stages of fever. From the experiments of Vogel it appears to be uric acid, either combined with an alkali, or modified by the presence of animal matter. Prout is of opinion that it contains some purpurate of ammonia; and, as he has detected the presence of nitric acid in the urine from which such sediments were deposited, he thinks it probable that the purpurate may be generated by the reaction of the uric and nitric acids on each other in the urinary passages.

Hippuric Acid.—Under this name, derived from *ἵππος* a horse, and *οὖρον* urine, Liebig has described a peculiar compound, which is deposited from the urine of the horse when it is mixed with hydrochloric acid in excess. The deposite, which is crystalline and of a yellowish-brown tint, is boiled with milk of lime, to which small quantities of chloride of lime are added, until the urinous odour ceases. It is then digested with animal charcoal; and on mixing the hot filtered solution with a large excess of hydrochloric acid, hippuric acid is deposited in cooling in rather large prisms, two or three inches in length, and beautifully white. It exists in the urine of most herbivorous animals united with soda. (An. de Ch. et de Ph. xliii. 188.)

Hippuric acid is analogous in its characters to benzoic acid, and was at first supposed to be that acid modified by the presence of animal matter; but Liebig contends that it is clearly distinguished from benzoic acid by the character of its salts, in being less soluble in water, and in containing nitrogen. It is composed of

	Carbon.	Hydrogen.	Nitrogen.	Oxygen.
In 100 parts	60.76	4.92	7.82	26.5
In equiv.	122.4 or 20 eq.+	9 or 9 eq.+	14.15 or 1 eq.+	48 or 6 eq. = 193.55.

Formic Acid.—A sour liquor exists in ants, which they eject when irritated, and which may be obtained in solution by bruising these insects into a pulp with water: the liquid was supposed by Fourcroy and Vauquelin to contain acetic and malic acids; but the experiments of Suersen, Gehlen, Berzelius, and Dobereiner have proved that it is a mixture of the malic with a peculiar volatile acid, distinct from acetic acid, and easily separable by distillation. The peculiar origin of this compound has suggested for it the name of *formic acid*. Dobereiner has shown that it is readily generated artificially by distilling a mixture of 1 part of tartaric acid, 1½ of peroxide of manganese, and 1½ of sulphuric acid diluted with about 2½ parts of water: a capacious retort should be used, as the materials froth up during the process. The tartaric acid receives oxygen from the manganese, and is resolved into water, carbonic acid, and formic acid. (An. of Phil. N. S. iv. 311.) Liebig and Gmelin have found that several other substances, such as sugar, starch, sugar of milk, and ligneous fibre, may be substituted for tartaric acid; but the formic acid is then accompanied by some foreign matter, which may be removed by neutralizing with an alkali, and decomposing the formate by sulphuric acid. Even alcohol may be used; but it must be employed in a dilute state, in order to prevent the production of sulphuric or formic ether. Formic acid, indeed, appears to be a frequent result of chemical changes, of which some examples were formerly mentioned (pages 269 and 499); and hence it is important to be well acquainted with its composition.

By these processes formic acid is procured in a very dilute state: it is obtained with less water by distilling a mixture of one part of water, two of strong sulphuric acid, and three of dry formate of potassa. But the free acid in its most concentrated form has not less than 19.6 per cent. of water, and a density of 1.1168. Formic acid is a feeble acid, has a sour taste and reaction, and its odour resembles that of acetic acid, but is attended with a peculiar pungency. With bases it forms crystallizable salts, by the form of which, especially of the formates of baryta, strontia, lime, and oxide of zinc, it is completely distinguished from acetic acid.

According to the analysis of formate of oxide of lead by Berzelius, the equivalent of this acid is inferred to be 37.24; and it is composed of 12.24 parts or two equivalents of carbon, 1 part or one equivalent of hydrogen, and 24 parts or three equivalents of oxygen. From the ratio of these elements, it is manifest that formic acid may be considered a compound of two equivalents of carbonic oxide and one equivalent of water, as expressed by the formula $2(C+O)+(H+O)$; and it is actually resolved into these compounds by being gently heated with strong sulphuric acid, carbonic oxide gas being disengaged. Warmed with peroxide of mercury it takes oxygen from the metal, and is resolved into water and carbonic acid, the latter of which escapes with effervescence. By these characters formic acid is distinguished from other acids.

Allantoic acid.—This compound, described by Buniva and Vauquelin under the name of *amniotic acid*, and said to exist in the *liquor amnii* of the cow, was found by Dzondi to be present solely in the liquor of the allantois, and to be in fact the urine of the fœtus. The mistake of the discoverers has also been corrected by Lassaigne. (An. de Ch. et de Ph. xxxiii. 279.)

The allantoic acid is obtained by gently evaporating the liquid of the allantois of the fœtal calf, when the acid is deposited in the form of white acicular crystals. It is very sparingly soluble in water, but yields with the alkalies soluble compounds which are decomposed by most of the acids. According to the analysis of Liebig, its elements are in the ratio of five equivalents of carbon, four of hydrogen, two of nitrogen, and four of oxygen.

Several other animal acids, such as the stearic, oleic, margaric, and others, should also be mentioned here; but as they are closely allied to the fatty principles from which they are derived, they will be more conveniently described in the following section.

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SECTION III.

ANIMAL OILS AND FATS.

The fatty principles derived from the bodies of animals are very analogous in composition and properties to the vegetable fixed oils; and in Britain, where the latter are comparatively expensive, the former are employed, both for the purpose of giving light, and for the manufacture of soap. Their ultimate elements are carbon, hydrogen, and oxygen; and most of them, like the fixed oils, consist of two or more definite compounds, such as stearine, margarine, and oleine, in a state of combination.

From a curious experiment of Bérard it appears that a substance very analogous to fat may be made artificially. On mixing together one measure of carbonic acid, ten measures of carburetted hydrogen, and twenty of hydrogen, and transmitting the mixture through a red-hot tube, several white crystals were obtained, which were insoluble in water, soluble in alcohol, and fusible by heat into an oily fluid. (An. of Ph. xii. 41.) Dobereiner prepared an analogous substance from a mixture of coal gas and aqueous vapour.

The annexed table shows the composition of several animal fats, and of their products when formed into soap. The analyses are by Chevreul, excepting that of stearine by Lecanu, of spermaceti by Bérard, and of ambreine by Pelletier.

	Carb.	Hyd.	Oxy.		Formulæ.
Human fat	79.000	+11.416	+ 9.584	=100	
Oleine of human fat	78.566	+11.447	+ 9.987	=100	
Hogslard	79.098	+11.146	+ 9.756	=100	
Oleine of hogslard	79.03	+11.422	+ 9.548	=100	
Mutton suet	78.996	+11.700	+ 9.304	=100	
Stearine of mutton suet	78.02	+12.2	+ 9.78	=100	$C^{78}H^{70}O^{7}$ or
	446.76	+70	+56	=572.76	$C^{70}H^{67}O^{5}+C^{8}H^{3}O^{2}$
Oleine of mutton suet	79.354	+11.09	+ 9.556	=100	

	Carb.	Hyd.	Oxy.		Formulæ.
Stearic acid (anhydrous)	80.145 428.4	+12.478 +67	+ 7.377 +40	=100 =535.4	$C^{70}H^{67}O^{5}$
Margaric acid (anhydrous)	79.053 428.4	+12.01 +65	+ 8.937 +48	=100 =541.4	$C^{70}H^{65}O^{6}$
Oleic acid (anhydrous)	80.942 428.4	+11.359 +58	+ 7.699 +40	=100 =526.4	$C^{70}H^{58}O^{5}$
Glycerine	40.071 18.36	+ 8.925 + 4	+51.004 +24	=100 = 46.36	$C^{3}H^{4}O^{3}$ or $C^{3}H^{3}O^{2}+\dot{H}$
Cetine .	81.660	+12.862	+ 4.578	= 99.1	
Spermaceti	79.5	+11.6	+ 8.9	=100	
Ethal .	79.766 97.92	+13.945 +17	+ 6.289 + 8	=100 =122.92	$C^{16}H^{17}O$ or $4C^{4}H^{4}+\dot{H}$.
Phocenic acid	65.00 61.2	+ 8.25 + 7	+26.75 +24	=100 = 92.2	$C^{10}H^{7}O^{3}$
Cholesterine	85.095	+11.88	+ 3.025	=100	
Ambreine	83.37	+13.32	+ 3.31	=100	

Train Oil.—Train oil is obtained by means of heat from the blubber of the whale, and is employed extensively in making oil gas, and for burning in common lamps. It is generally of a reddish or yellow colour, emits a strong unpleasant odour, and has a considerable degree of viscidity, properties which render it unfit for being burned in Argand lamps, and which are owing partly to the heat employed in its extraction, and partly to the presence of impurities. By purification, indeed, it may be rendered more limpid, and its odour less offensive; but it is always inferior to spermaceti oil.

Spermaceti Oil is obtained from an oily matter lodged in a bony cavity in the head of the *Physeter macrocephalus*, or spermaceti whale. On subjecting this substance to pressure in bags, a quantity of pure limpid oil is expressed; and the residue, after being melted, strained, and boiled with a solution of potassa, is sold under the name of *spermaceti*. This principle is probably modified in the process by which it is purified.

Animal Oil of Dippel.—This name is applied to a limpid volatile oil, which is entirely different from the oils above mentioned, and is a product of the destructive distillation of animal matter, especially of albuminous and gelatinous substances. When purified by distillation, it is clear and transparent. It was formerly much used in medicine, but is now no longer employed.

Human Fat.—This variety of fat has a yellowish colour, is inodorous, fuses at a very gentle heat, and retains its fluidity at 59°: that of the loins begins to solidify at 77° and it is quite solid at 63°. It requires for solution 40 parts of hot alcohol, which in cooling deposites stearine of a peculiar kind, leaving oleine in solution. When saponified it yields margaric and oleic acids and glycerine, but no stearic acid.

Hogslard.—This fat is of a nearly white colour, and the fusing point of different varieties between 79° and 88°. It probably contains both the stearine and margarine besides oleine. When saponified, it yields margaric, stearic, and oleic acids, and glycerine.

Suet.—This term is applied to the fat situated about the loins and kidneys, which is less fusible than the fat from other parts of the same animal. The suet from the ox and sheep is principally used: when separated by fusion from the membrane in which it occurs, it is called tallow, and is extensively employed in the manufacture of soap and candles. Beef and mutton suet resemble hogslard in their constituents and in the products of saponification. Beef suet, when fused, congeals at 102°, and mutton suet at 98° or a few degrees higher.

Stearine.—This compound is a constituent of several animal fats, especially of hogslard and suet, the latter of which contains one-fifth of stearine. It is prepared by fusing mutton suet in a flask, agitating with its own weight of ether, and when the whole is cold separating the soluble parts by pressure in a cloth and in bibulous paper. This process is repeated until the parts soluble in cold ether are removed. The insoluble part is stearine. It may also be prepared by mixing essence of turpentine with fused mutton suet, and when the mass has cooled pressing out the fluid parts by bibulous paper: the solid part left after repeated fusion with turpentine is stearine, which should be purified by solution in hot ether to remove adhering turpentine.

Pure stearine, as separated from its ethereal solution, and dried by compression in bibulous paper, occurs in small white brilliant laminæ, and fuses at 129° into a mass like wax, but so friable that it may be reduced to powder. It dissolves in boiling strong alcohol, but separates on cooling in snow-white flakes. Boiling ether dissolves it in large proportion, but when cold retains an 1-225th of its weight. When sharply heated, it is decomposed, and among other products it yields stearic acid. When digested in pure potassa, it is entirely resolved into stearic acid and glycerine, both regarded as anhydrous. This will be obvious by the formulæ of pages 596 and 597. Stearine may be regarded as a compound of stearic acid and glycerine, and its conversion into soap as the mere separation of glycerine, which, in the act of quitting the stearic acid, combines with one eq. of water. The foregoing facts are drawn from a late essay by Lecanu. (An. de Ch. et de Ph. lv. 192.)

Margarine.—After the stearine in the foregoing process has been deposited, another solid fatty principle, which Lecanu terms *margarine*, may be obtained by allowing the ethereal solution to evaporate spontaneously. To free it from adhering ether and oleine, it should be pressed between folds of bibulous paper. Margarine is very similar in its properties to stearine, but is distinguished from it by its greater fusibility, its point of fusion being 117½°, and by its ready solubility in cold ether. With an alkali it yields stearic acid and glycerine.

The solid matter of vegetable oils is not identical with the stearine of suet, as was thought by Chevreul, but appears from the late experiments of Lecanu to be more closely allied to the margarine of suet. It differs, however, from both by yielding margaric and oleic, and not stearic, acid when converted into soap.

Oleine.—The liquid matter of animal fats, obtained by compression in bibulous paper, is very similar to the oleine obtained in a similar manner from frozen vegetable oils.

Margaric and Oleic Acids.—When the fats above mentioned, or the fixed vegetable oils, are boiled with a solution of potassa or soda, the elements of the fat or oil undergo a new arrangement, whereby, without losing any gaseous substance or absorbing any from the air, they are converted into one or more fatty acids and glycerine. To this change the elements of water contribute. The new acids combine with the alkali and constitute soap, which after due evaporation collects on the surface of the water, while the glycerine remains in solution. The acids which, in ordinary soap, are united with potassa or soda as compounds soluble in water, form insoluble compounds with most other metallic oxides; and hence it is that solutions of soap are precipitated by salts of lime, oxide of lead, and similar metallic solutions. These insoluble soaps may be formed directly by digesting oleaginous substances with water and metallic oxides.

The margaric and oleic acids are best prepared from soap made with potassa and fluid vegetable oil. This soap, after being well dried, is treated by successive portions of cold alcohol of sp. gr. 0.821, in which the oleate of potassa is soluble and the margarate insoluble. The two salts, thus separated, are decomposed by means of an acid.

Margaric acid, so named from its pearly lustre (from *μαργαριτης a pearl*) is insoluble in water, and is hence precipitated by acids from the solution of its salts. It is abundantly dissolved by hot alcohol, and is deposited from the saturated solution, on cooling, in a crystalline mass of a pearly lustre. At 140° it is fused, and shoots into brilliant white acicular crystals as it cools. It has an acid reaction, and its salts, those of the alkalies excepted, are very sparingly soluble in water. The crystallized acid contains 3.4 per cent. of water, corresponding to two eq. of water, from which it can only be separated by combining with an alkaline base.

Oleic acid is best prepared from soap made with linseed oil and potassa, since the greater part of it consists of the oleate of that alkali. This salt is first separated from margarate of potassa by cold alcohol, and the oleic acid then precipitated from an aqueous solution of the oleate by means of an acid. At the mean temperature oleic acid is a colourless oily fluid, which congeals when it is cooled to near zero. It has a slightly rancid odour and taste, and reddens litmus paper. Its specific gravity is 0.898. It is insoluble in water, but is dissolved in every proportion by alcohol. Of the neutral oleates hitherto examined, those of soda and potassa are alone soluble in water.

In its free state it contains 3.8 per cent., corresponding to one equivalent of water, which it loses in uniting with most metallic oxides.

Stearic Acid.—This acid is best prepared by converting pure stearine into soap, and decomposing the resulting stearate with an acid. It is very similar in its appearance and properties to margaric acid, the principal distinction being a difference of fusibility, the fusing point of stearic acid being 158°. The crystallized acid consists of one eq. of anhydrous stearic acid and one eq. of water.

Sebacic Acid.—Thenard has applied this name to an acid which is obtained by the distillation of hogslard or suet, and is found in the recipient mixed with acetic acid and fat, partially decomposed. It is separated from the latter by means of boiling water, and from the former by acetate of oxide of lead. The sebacate of that oxide, which subsides, is subsequently decomposed by sulphuric acid.

Sebacic acid reddens litmus paper, dissolves freely in alcohol, and is more soluble in hot than in cold water. It melts like fat when heated, and crystallizes in small white needles in cooling. It is not applied to any use.

Butyrine.—Butter differs from the common animal fats in containing a peculiar oleaginous matter, which is quite fluid at 70°, and to which Chevreul has applied the name of *butyrine.* When converted into soap, it yields, in addition to the usual products, three volatile odoriferous compounds, namely, the *butyric*, *caproic*, and *capric* acids.

Phocenine is a peculiar fatty substance contained in the oil of the porpoise (*Delphinus phocæna*) mixed with oleine. When converted into soap, it yields a volatile odoriferous acid, called the *phocenic acid.* (Chevreul.)

Hircine is contained in the fat of the goat and sheep, and yields the *hircic acid* when converted into soap. (Chevreul.)

Other acids, more or less analogous to those above described, are formed during the conversion of other oleaginous substances into soap. Thus, castor oil yields three acids, to which Bussy and Lecanu have applied the names of *margaritic*, *ricinic*, and *elaiodic* acid. The *cevadic* acid was prepared in a similar manner by Pelletier and Caventou from oil derived from the seeds of the *Veratrum sabadilla;* and the same chemists have given the name of *jatrophic* acid (more properly *crotonic*) to the acid of the soap made from croton oil. This oil is derived from the seeds of the *Croton tiglium.*

Glycerine.—The sweet principle of oils, *glycerine* of Chevreul, was discovered by Scheele. It was originally obtained in the formation of common plaster by boiling oil with oxide of lead and a little water; and Chevreul found that it is produced during the saponification of fatty substances in general. In preparing soap by means of potassa, the glycerine is left in the mother liquor; and on neutralizing the free alkali with sulphuric acid, evaporating to the consistence of syrup, and treating the residue with alcohol, it is dissolved. The alcoholic solution, when evaporated, yields glycerine in the form of an uncrystallized syrup. It is soluble in water and alcohol, and has a sweet taste, but is not susceptible either of the vinous or acetous fermentation.

Spermaceti.—This inflammable substance, which is prepared from the spermaceti whale, as above mentioned, commonly occurs in crystalline plates of a white colour and silvery lustre. It is brittle, and feels soft and slightly unctuous to the touch. It has no taste, and scarcely any odour. It is insoluble in water, but dissolves in about thirteen times its weight of boiling alcohol, from which the greater part is deposited on cooling in the form of brilliant scales. It is still more soluble in ether. It is exceedingly fusible, liquefying at a temperature which is distinctly below 212°.

The spermaceti of commerce always contains some fluid oil, from which it may be purified by solution in boiling alcohol. To the white crystalline scales deposited from the spirit as it cools, and which is spermaceti in a state of perfect purity, Chevreul has given the name of *cetine.*

Ethal.—When cetine is boiled with alkalies it is slowly and incompletely saponified, since, in addition to margaric and oleic acid, a solid fatty principle is generated, amounting to 40.64 per cent. of the cetine used. Chevreul gave it the name of *ethal*, from the first syllable of the words ether and alcohol, because of its analogy to those liquids in point of composition (page 597). Ethal congeals after fusion at 86°, and at 124° under water. It is soluble in every proportion in strong alcohol at 130°, and may be distilled without change.

Adipocire.—When a piece of fresh muscle is exposed for some time to the action of water, or is kept in moist earth, the fibrin entirely disappears, and a fatty matter called *adipocire* remains, which has some resemblance to spermaceti. The fibrin was formerly thought to be really converted into adipocire; but Gay-Lussac* and Chevreul maintain that this substance proceeds entirely from the fat originally present in the muscle, and that the fibrin is merely destroyed by putrefaction. Dr. Thomson maintains, however, that the conversion of fibrin into fat does occur in some instances, and has related a remarkable case in proof of his opinion. (An. of Phil. vol. xii. p. 41.) According to M. Chevreul, the adipocire is not a pure fatty principle, but a species of soap, chiefly consisting of margaric acid in combination with ammonia generated during the decomposition of the fibrin.

Cholesterine.†—This name is applied by Chevreul to the crystalline matter which constitutes the basis of most of the biliary concretions formed in the human subject. Fourcroy, regarding it as identical with spermaceti and the fatty matter just described, comprehended all these circumstances under the general appellation of adipocire; but Chevreul has shown that it is an independent principle, wholly different from spermaceti.

Cholesterine is a white brittle solid of a crystalline lamellated structure and brilliant lustre, very much resembling spermaceti; but it is distinguished from that substance by requiring a temperature of 278° for fusion, and by not being convertible into soap when digested in a solution of potassa. It is free from taste and odour, and is insoluble in water. It dissolves freely in boiling alcohol, from which it is deposited on cooling in white pearly scales.

When heated with its own weight of concentrated nitric acid, cholesterine is dissolved with disengagement of nitric oxide gas; and in cooling a yellow matter subsides, an additional quantity of which may be obtained by dilution with water. This substance possesses the properties of acidity, and is called *cholesteric* acid. It is insoluble in water, but dissolves freely in alcohol, especially with the aid of heat. Its taste is slightly styptic, and its odour somewhat like that of butter; it is lighter than water, and fusible at 136⅓° F. In mass it is of an orange-yellow tint; but when the alcoholic solution is evaporated spontaneously, it is deposited in acicular crystals of a white colour. It reddens litmus paper, and neutralizes alkaline bases. The cholesterates of potassa and soda are deliquescent and very soluble in water, but insoluble in alcohol and ether. The cholesterates of the earths and other metallic oxides are either sparingly dissolved by water or altogether insoluble. Its salts are precipitated by the mineral and most of the vegetable acids; but are not decomposed by carbonic acid. For these facts respecting the formation and properties of cholesteric acid, we are indebted to the experiments of Pelletier and Caventou. (Journal de Pharmacie, iii. 292.)

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* An. de Ch. et de Ph. vol. iv.

† From χολη *bile*, and στερεος *solid.*

Cholesterine has been detected in the bile of man, and of several of the lower animals, such as the ox, dog, pig, and bear. This interesting discovery was made about the same time by Chevreul in Paris, and by Tiedemann and Gmelin in Heidelberg. Lassaigne has likewise found it in the biliary calculus of a pig. (An. de Ch. et de Ph. xxxi.) It is frequently formed in parts of the body quite unconnected with the hepatic circulation, and appears to be a common product of deranged vascular action. Caventou, in the Journal de Pharmacie for October 1825, states that the contents of an abscess, formed under the jaw, apparently in consequence of a carious tooth, were found by him to consist almost entirely of cholesterine. In the article *Calcul* of the *Nouveau Dictionnaire de Médecine*, M. Breschet observes that cholesterine has been found in cancer of the intestines, and in the fluid of hydrocele and ascites in the human subject; and he adds that M. Barruel procured it in large quantity from an ovarian cyst in a mare, and in the fluid drawn off from the ovary of a woman, and scrotum of a man. Breschet has found it also in a tumour under the tongue. Dr. Christison found it in the fluid of hydrocele, taken from a patient in the Royal Infirmary of Edinburgh by the late Dr. William Cullen; in an osseous cyst, into which the kidneys of another patient were converted; and in the membranes of the brain of an epileptic patient. Reichenbach has detected it in animal tar, whence it would seem to be a product of the destructive distillation of animal matter.

The best method of preparing pure cholesterine is to treat human biliary concretions, reduced to powder, with boiling alcohol, and to filter the hot solution as rapidly as possible. As the liquid cools, the greater part of the cholesterine subsides. In this way it is freed from the colouring matter with which it is commonly associated in the gall-stone.

Ambergris.—This substance is found floating on the surface of the sea near the coasts of India, Africa, and Brazil, and is supposed to be a concretion formed in the stomach of the spermaceti whale. It has commonly been regarded as a resinous principle; but its chief constituent is a substance very analogous to cholesterine, and to which Pelletier and Caventou have given the name of *ambreine.* By digestion in nitric acid, ambreine is converted into a peculiar acid called the *ambreic acid.* (An. of Phil. vol. xvi.)

MORE COMPLEX ANIMAL SUBSTANCES, AND SOME FUNCTIONS OF ANIMAL BODIES.

SECTION I.

BLOOD, RESPIRATION, AND ANIMAL HEAT.

Blood.

The blood is distinguished from other animal fluids by its colour, which is a florid red in the arteries and of a dark purple tint in the veins. Its taste is slightly saline, its odour peculiar, and to the touch it seems somewhat unctuous. Its specific gravity is variable, but most commonly it is near 1.05; and in man its temperature is about 98° or 100° F. While flowing in its vessels, or when recently drawn, it appears to the naked eye as a uniform homogeneous liquid; but if examined with a microscope of sufficient power, numerous red particles of a globular form are seen floating in a nearly colourless fluid. Hence the blood, while circulating, is mechanically distinguishable into two parts, one essentially liquid, which may be called *liquor sanguinis*, and the other essentially solid, which is merely suspended in the former, and imparts its red colour to the mixture.

Both of these constituents of the blood are complex substances. The red globules, discovered by Leuwenhoeck and carefully examined by Hewson, were observed by the late Dr. Young to consist of two parts, a colourless globule insoluble in water, and a red colouring matter soluble in that menstruum. The observations of Mr. Bauer, coinciding with those of Young, led to the belief that the entire red globule consists of a central smaller globule of fibrin, which is surrounded with a pellicle or film of colouring matter: the coloured globules manifest no tendency to cohere; but the nuclei of fibrin, when deprived of their colouring envelope, which they soon lose after the blood is drawn, adhere together with great facility. (Phil. Trans. 1818, p. 172.) These remarks have been corroborated by Prevost and Dumas, who extended their researches to the blood of various animals; and they further observed that in birds and the cold-blooded tribes the globules are elliptical, while they are spherical in mammiferous animals.

The *liquor sanguinis*, considered by some as serum, has been shown by Dr. Benjamin Babington, in a short essay replete with sound observation, to be very similar to chyle, and to consist of fibrin, *held in solution*, along with albuminous, oleaginous, and saline matter, by the water of the blood. When set at rest the *liquor sanguinis* coagulates, yielding a uniform jelly of precisely the same volume as when it was liquid, and possessing the exact figure of the containing vessel; and in a short time, by the contraction of the mass of coagulated fibrin, a yellowish liquid appears, which is the *serum* of the blood. The microscopical observations of Mr. Bauer, cited by the late Sir E. Home in the Croonian lecture for 1818 (Phil. Trans. 1819, p. i.), prove that, during this process, numerous globules, smaller than the colourless nuclei of the red globules, are generated, and give rise to coagulation by mutual adhesion. Though the production of these globules is most abundant soon after the blood is drawn, yet their developement continues for several days; Mr. Bauer observed them to appear in the clear serum of a sheep 8 or 10 days after removal from the animal; and Mr. Faraday made the same observation with the serum of human blood.

It is the liquor sanguinis, thus shown to be spontaneously separable into fibrin and serum, which forms a yellowish liquid stratum at the surface of blood recently drawn from persons in acute rheumatism or other inflammatory fevers. In such affections the liquor sanguinis, from causes not at all understood, generally coagulates with unusual slowness, so that the heavier red globules have time to subside to an appreciable extent, leaving an upper stratum of nearly colourless fluid, which by the cautious use of a spoon may be removed and collected in a separate vessel. The *buffy coat* of such blood is the pure fibrin separated by coagulation from the liquor sanguinis. The *coagulable lymph* of Surgeons, which is thrown out on cut surfaces, appears to be the liquor sanguinis; and this fluid is also not unfrequently exhaled in dropsies, when the fibrin either constitutes a gelatinous deposite, or appears as white flakes floating in the serous fluid. It is poured out by the intestines during an attack of cholera, the rice-water fluid characteristic of that disease consisting of a saline and albuminous solution, in which numerous shreds of fibrin are suspended.

When blood drawn from a healthy person is set at rest, it speedily coagulates, and is found after a few hours to have separated itself into two parts, one the serum identical with that obtained from the liquor sanguinis, and the other a uniformly red coagulum called the *clot*, *cruor*, or *crassamentum*. The uniform redness of the clot is owing to the fibrin coagulating before the red globules have had time to subside. It contains the colouring matter of the blood, together with all the fibrin, except traces held in solution in the serum, as well that which had formed part of the liquor sanguinis, as the fibrinous nuclei of the red globules. The ratio of the clot and serum is very variable, and by no means represents the quantity of fibrin or colouring matter contained in the blood. Dr. B. Babington has shown, in the essay already referred to, that the ratio materially depends on the figure of the containing vessel:—two portions of blood were drawn from the same person, one being received and allowed to coagulate in a pear-shaped bottle, and the other in a pint basin; and the ratio of serum to clot was as 1000 to 1292 in the former, and as 1000 to 1717 in the latter. In fact, when a mass of coagulating blood is contained in a spherical vessel, the particles of fibrin being little removed from a common centre are more powerfully attracted towards each other, yield a denser clot, and squeeze out more serum, than when the coagulation takes place in a shallow wide basin, where the particles are spread over a large surface. The clot of the former is compact and small; while that of the latter, being spongy, and hence retaining much serum within it, is large and abundant, though the actual quantity of solid matter is the same in both.

The following table exhibits the results of two careful analyses of the blood by Lecanu:—(An. de Ch. et de Ph. xlviii. 308.)

Water	780.145	785.590
Fibrin	2.100	3.565
Colouring matter	133.000	119.626
Albumen	65.090	69.415
Crystalline fatty matter	2.430	4.300
Oily matter	1.310	2.270
Extractive matter soluble in water and alcohol	1.790	1.920
Albumen combined with soda	1.265	2.010
Chloride of sodium	8.370	7.304
———— potassium		
Carbonates of potassa and soda		
Phosphates of potassa and soda		
Sulphates of potassa and soda		
Carbonates of lime and magnesia	2.100	1.414
Phosphates of lime, magnesia, and iron		
Peroxide of iron		
Loss	2.400	2.586
	1000.000	1000.000

The earthy salts were obtained by incinerating the albumen, and the trace of iron was obviously derived from a little colouring matter of the blood. Fatty matter appears to be always present in serum, having been found by Dr. B. Babington as well as by Lecanu: the former obtained it by agitating serum repeatedly but gently with ether, which took up the fatty substance, and left it by evaporation; while the latter mixed the serum with alcohol, and dissolved the fatty principles from the alcoholic extract by means of ether. The oily matter of the serum is very soluble in ether and cold alcohol, is liquid at common temperatures, and is readily converted into soap by potassa. The crystalline fatty matter is similar in appearance to cholesterine, resists the action of potassa, and is soluble in ether and boiling alcohol: it appears to contain nitrogen as one of its elements.

The relative proportion of the ingredients of the blood must necessarily vary independent of disease even in the same individual, according as the nutrition is scanty or abundant. According to Lecanu slight variations arise from difference of age and sex, and the following comparative view is the mean of his analysis made with blood drawn from ten women and from ten men.

	Female.	Male.
Water	804.37	789·32
Albumen	69.72	67.50
Saline and extractive matter	9.95	10.69
Red globules	115.96	132.49
	1000.00	1000.00

In addition to the constituents of the blood already enumerated, M. Barruel declares that this fluid contains a volatile principle, peculiar to each species of animal. This principle has an odour resembling that of the cutaneous or pulmonary exhalation of the animal, and serves as a distinctive character by which the blood of different animals may be recognized. It is dissolved in the blood, and its odour may be perceived when the blood or its serum is mixed with strong sulphuric acid. The odour is commonly stronger in the male than in the female. In man it resembles the human perspiration; in the ox, it smells like oxen or a cow-house; and the odour from horses' blood is similar to that of their perspiration. (Journ. of Science, vi. N. S. 187.) Should the accuracy of these observations be confirmed, they may be advantageously applied in some cases of legal medicine.

Minute portions of alumina, silica, and manganese have been detected in the blood, and Dr. O'Shaughnessy confirms the statement of M. Sarzeau that a trace of copper may likewise be found; but the extremely minute quantity in which these substances occur, renders it doubtful whether they really exist in the blood, or are casually introduced in the course of analysis. Dr. Clanny reports the existence of a large quantity of *free* carbon in the blood; but I am not aware that the statement is borne out by experiment, and it is entirely opposed to the observation of other chemists. Of the presence of free carbonic acid in the blood, I shall have occasion to speak while discussing the subject of respiration.

Serum of the Blood.—This liquid, which separates during the coagulation of the blood, has a yellowish colour, is transparent when carefully collected, has a slightly saline taste, and is somewhat unctuous to the touch. Its average specific gravity is about 1.029. It has a slight alkaline reaction with test paper, owing to the presence of soda, which some chemists believe to be combined with carbonic acid, and others with albumen: the last opinion is the more probable, since serum, when agitated with carbonic acid, absorbs that gas in considerable quantity. Like other albuminous liquids, it is coagulated by heat, acids, alcohol, and all other substances which coagulate albumen. On subjecting the coagulum prepared by heat to gentle pressure, a small quantity of a colourless limpid fluid, called the *serosity*, oozes out, which contains, according to Dr. Bostock, about 1-50th of its weight of animal matter, together with a little chloride of sodium. Of this animal matter a portion is albumen, which may easily be coagulated by means of galvanism; but a small quantity of some other principle is present, which differs both from albumen and gelatin. (Medico-Chir. Trans. ii. 166.)

The composition of the serum, according to the late analysis of Lecanu, may be seen from his analysis of the blood, abstracting the colouring matter and fibrin which are foreign to it (page 603). The late Dr. Marcet found that 1000 parts of the serum of human blood are composed of water 900 parts, albumen 86.8, muriate of potassa and soda 6.6, muco-extractive matter 4, carbonate of soda 1.65, sulphate of potassa 0.35, and of earthy phosphates 0.60. This result agrees very nearly with that obtained by Berzelius, who states that the *extractive matter* of Marcet is lactate of soda united with animal matter. (Medico-Chir. Trans. iii. 231.)

Colouring Matter of the Blood.—This substance, to which the term *hematosine* is now applied, is so analogous in most of its chemical relations to albumen, that its complete separation from it is attended with great difficulty. It is obtained nearly pure by cutting the clot of blood into very thin slices with a sharp knife, as advised by Berzelius, soaking them repeatedly in distilled water, and letting them drain on bibulous paper after each immersion: the slices are then broken up in distilled water with a stick, briskly stirring in order to dissolve the colouring matter; and the filtered solution is evaporated to dryness in shallow capsules or dishes at a temperature of 80° or 100° F. As thus prepared the colouring matter, or hematosine, is soluble and possessed of all its characters; but it retains a little serum. It may be still further purified by the method of Engelhart, which is founded on the fact that hematosine is more coagulable by heat than albumen: serum diluted with ten parts of water does not coagulate at 160°; whereas hematosine, dissolved in fifty parts of water, begins to coagulate at 149°, and is thrown down in insoluble flocks of a brown colour. Unfortunately, however, its characters are changed by this operation, uncoagulated and coagulated hematosine bearing the same relation to each other as soluble and insoluble albumen. For the purpose of ultimate analysis the pure insoluble hematosine should be employed; but for examining the properties of hematosine, its less pure but soluble state is preferable.

Soluble hematosine, when quite dry, is black, with a lustre like jet in mass and red in powder or in thin layers, is insipid to the taste, and inodorous. In cold water it readily dissolves, forming a red liquid, which may be preserved without change for months. Its solution, like that of albumen, may be coagulated by heat as already mentioned; but when quite dry it may be heated to 212° without being rendered insoluble. Alcohol and acids likewise precipitate it: the latter deepen its tint, and fall in combination with it; but the compounds of hematosine with the muriatic, sulphuric, and acetic acid may be dissolved in water by means of an excess of their acid. The alkalies do not precipitate the aqueous solution of hematosine; but its solution in hydrochloric acid yields red flocks on the addition of ammonia. With some of the metallic oxides it forms insoluble compounds, especially with the oxides of tin and mercury; and hence the salts of these metals precipitate hematosine. In most of these properties, colour excepted, it resembles albumen; but Lecanu has indicated two pointed differences:—1. a solution of hematosine is not precipitated by the acetate or subacetate of oxide of lead, while both of these salts throw down albumen; 2. the precipitate occasioned by hydrochloric acid, when pressed between folds of linen to remove adhering acid and well dried, is soluble in strong boiling alcohol, whereas the corresponding compound of albumen and hydrochloric acid is quite insoluble. By this character Lecanu found that hematosine, carefully prepared from human blood, contains very little albumen; but that the colouring matter of blood from the ox and sheep appears to be a compound, in nearly equal parts, of hematosine and albumen. (An. de Ch. et de Ph. xlv. 5.)

Hematosine, according to the analysis of Michaelis, consists of carbon, hydrogen, nitrogen, and oxygen, very nearly in the same ratio as in fibrin and albumen; but it differs from both in containing iron. This was announced in 1806 by Berzelius in his comparative examination of the ingredients of the blood (Medico-Chir. Trans. iii. 213): from the albumen and fibrin he could obtain no iron; but 100 parts of hematosine, when burned in the open air, left 1.25 of ashes, containing 0.625 of oxide of iron, and 0.625 of a mixture of carbonate and phosphate of lime, phosphate of magnesia, and subphosphate of oxide of iron. He was unable to detect the presence of iron by any of the liquid tests. These facts, though questioned by other chemists, were fully established by Dr. Engelhart, who gained the prize offered in the year 1825 by the Medical Faculty of Gottingen for the best Essay on the nature of the colouring matter of the blood (Edinb. Med. and Surg. Journ. for January, 1827). He demonstrated that the fibrin and albumen of the blood, when carefully separated from colouring particles, do not contain a trace of iron; and, on the contrary, he procured iron from the red globules by incineration. But he likewise succeeded in proving the existence of iron in the colouring matter of the blood by the liquid tests; for, on transmitting a current of chlorine gas through a solution of the red globules, the colour entirely disappeared, white flocks were thrown down, a a transparent solution remained, in which peroxide of iron was discovered by all the usual reagents. The results obtained by Dr. Engelhart, relative to the quantity of the iron, correspond with those of Berzelius. These facts have been since confirmed by Rose, who has accounted in a satisfactory manner for the failure of former chemists in detecting iron in the blood while in a fluid state. He finds that oxide of iron cannot be precipitated by the alkalies, hydrosulphuret of ammonia, or infusion of galls, if it is dissolved in a solution which contains albumen or other soluble organic principles.

From the presence of iron in hematosine, and its total absence in the other principles of the blood, chemists were induced to suspect that its peculiar colour was in some way or other produced by that metal, an idea which received additional support from the known tendency of peroxide of iron to form salts of a red colour. But this view, though plausible on these grounds, is in other respects improbable. The real state in which iron exists in the blood is quite unknown, and its minute proportion seems unequal to produce so intense a colour as that of the blood. The only probable mode of explaining the diversity of tints which agents of different kinds produce in the blood, is to adopt the opinion ably maintained by Mr. Brande, who supposes that the tint of hematosine is owing to a peculiar animal colouring principle, capable like cochineal or madder of acting as a dye, and of combining with metallic oxides. He succeeded in obtaining a compound with hematosine and oxide of tin; but it yields the finest lakes with nitrate of peroxide of mercury and corrosive sublimate. Woollen cloths impregnated with either of these compounds, and immersed in an aqueous solution of hematosine, acquired a permanent red dye, unchangeable by washing with soap. (Phil. Trans. 1812.)

Fibrin of the Blood.—Fibrin appears to exist in the blood in two states, as already mentioned;—as the central nuclei of the red globules, and in solution in the serum. The fibrin from both sources is obtained by beating up the clot of blood with successive portions of water, so as to dissolve all the serum and colouring matter, leaving the insoluble fibrin quite white; but the best mode of separation is to stir recently drawn blood with a stick during coagulation, when the fibrin adheres to it in strings, which are easily rendered colourless by washing.

Coagulation of the Blood.—This phenomenon is occasioned by the agglutination of the fibrin of the blood,—both of the nuclei of the red globules, after they have lost their colouring envelope, and of that part which is in solution. The time required for coagulation is influenced by temperature, being promoted by heat, and retarded by cold. Sir C. Scudamore finds that blood which begins to coagulate in four minutes and a half in an atmosphere of 53°, undergoes the same change in two minutes and a half at 98°; and that which coagulates in four minutes at 98° will become solid in one minute at 120°. On the contrary, blood which coagulates firmly in five minutes at 60° will remain quite fluid for twenty minutes at the temperature of 40°, and requires upwards of an hour for complete coagulation. (Scudamore on the Blood.)

The process of coagulation is influenced by exposure to the air. If atmospheric air be excluded, as by filling a bottle completely with recently drawn blood, and closing the orifice with a good stopper, coagulation is retarded. It is singular, however, that if blood be confined within the exhausted receiver of an air-pump, the coagulation is accelerated. (Scudamore.)

Recently drawn blood, owing doubtless to its temperature, is known to give off a portion of aqueous vapour, which has a peculiar odour, indicative of the presence of some peculiar principle, but in which nothing but water can be detected. Physiologists are not agreed upon the question whether the act of coagulation is or is not accompanied with disengagement of gaseous matter. In the experiments of Vogel, Brande, and Scudamore, blood coagulating in the vacuum of an air-pump was found to emit carbonic acid, and Scudamore even inferred that the evolution of this gas constitutes an essential part of the process. Other experimentalists, however, have obtained a different result. Dr. John Davy and the late Dr. Duncan, jun., failed in their attempts to procure carbonic acid from blood during coagulation; and Dr. Christison, in an experiment which I witnessed, was not more successful. This evidence seems positive against the notion that the evolution of carbonic acid gas is an essential part of coagulation. The existence of carbonic acid in *venous* blood, is a different question, and this point will be discussed under the head of respiration.

Coagulation is influenced by the rapidity with which the blood is removed from the body. Sir C. Scudamore observed, that blood slowly drawn from a vein coagulates more rapidly than when taken in a full stream.

Experiments are still wanting to show the influence of different gases on coagulation. Oxygen gas accelerates coagulation, and carbonic acid retards but cannot prevent it.

Heat is evolved during the coagulation of the blood. The late Dr. Gordon estimated the rise of the thermometer at six degrees; and Dr. Davy, on the other hand, regards the increase of temperature from this cause as very slight. Sir C. Scudamore finds that the rate at which blood cools is distinctly slower than it would be were no caloric disengaged, and he observed the thermometer to rise one degree at the commencement of coagulation.

Some substances prevent the coagulation of the blood. This effect is produced by a saturated solution of chloride of sodium, hydrochlorate of ammonia, nitre, and a solution of potassa. The coagulation, on the contrary, is promoted by alum and the sulphates of the oxides of zinc and copper. The blood of persons who have died a sudden violent death, by some kinds of poison, or from mental emotion, is usually found in a fluid state. Lightning is said to have a similar effect; but Sir C. Scudamore declares this to be an error. Blood, through which electric discharges were transmitted, coagulated as quickly as that which was not electrified; and in animals killed by the discharge of a powerful galvanic battery, the blood in the veins was always found in a solid state.

The cause of the coagulation of the blood has been the subject of much speculation to physiologists. The tendency of this fluid to preserve the liquid form while contained in a living animal, cannot be ascribed to the motion to which it is continually subject within the vessels. It is a familiar fact that blood, though continually stirred out of the body, is not prevented from coagulating; and it has been noticed, that the coagulation of blood which is set at rest within its proper vessels by the application of ligatures, or which has been accidentally extravasated within the body, is materially retarded. It has, indeed, been hitherto found impossible to account in a satisfactory manner for the blood retaining fluidity by reference to motion, temperature, or the operation of any physical or chemical laws; and, consequently, it is generally ascribed to the agency of the vital principle. The blood is supposed either to be endowed with a principle of vitality, or to receive from the living parts with which it is in contact a certain vital impression, which, together with constant motion, counteracts its tendency to coagulate.

Blood in Disease.—The blood may be diseased either by the excess or deficiency of one or more of its proper constituents, or from the presence of substances which are foreign to it. One familiar instance of diseased blood is jaundice, when bile enters the circulation and is distributed to every organized part of the body. Though the presence of bile in the blood during jaundice has been detected, yet its passage into the circulating mass appears so rapidly succeeded by its exit, that its detection in the blood itself is generally difficult. Urea has also been detected, sometimes in very large quantity: it appears to be constantly present in the blood, whenever the secretion of urine is suppressed. Prevost and Dumas wholly arrested the secretion of urine in a dog by tying the renal vessels and excising the kidneys, and two days after the operation they obtained 20 grains of urea from 5 ounces of his blood. (An. de Ch. et de Ph. xxxiii. 90.) Dr. Christison found urea in the blood of persons suffering under renal disease, as will be mentioned in th section on the urine; and Dr. Prout appears also to have made a similar observation. The serum of the blood in this affection has usually a lower sp. gr. than healthy serum, the average of several cases being 1.021 (Gregory); and the albumen is in smaller proportion than natural. Urea has been detected by Dr. O'Shaugnessy in the blood of persons labouring under cholera, in which disease the action of the kidneys is generally very much disturbed. The sp. gr. of the serum of diabetic blood is usually above the natural standard, being so high as 1.0354. (Marcet).

The serum of blood, instead of being transparent, as it commonly is, has sometimes a cloudy appearance like whey, and in some more rare instances is perfectly opaque and white, as if it had been mixed with milk. The cause of the opacity has been experimentally examined by Drs. Traill and Christison, who have traced it to the presence of oleaginous matter, which the latter has shown to contain both stearine and elaine, and to be very similar to human fat. The milkiness may, therefore, be ascribed to fat being mechanically diffused through the serum like oil in an emulsion. It may be easily separated by agitating the serum in a tube with half its bulk of sulphuric ether, when the adipose matter is instantly dissolved, the opacity in consequence disappears, and on evaporating the clear ethereal solution, which rises to the surface of the mixture, the fat is obtained in a separate state. By this means he procured on one occasion five per cent. of fat from milky serum, and one per cent. from serum which had the aspect of whey. (Edinb. Med. and Surg. Journal, April, 1830.)

The most remarkable kind of diseased blood which has yet been studied by chemists is that which occurs in cholera. During the progress of that disease an enormous discharge takes place of a whitish-coloured fluid similar to a mixture of boiled rice with water, an appearance occasioned by a white flaky matter floating in a nearly colourless liquid. The insoluble part has the character of fibrin: while the liquid portion is a weak solution of albumen, is faintly alkaline, and contains the same kind of salts as exist in the blood. On examining the blood itself, it is found to contain less water and more albumen and hematosine than healthy blood; the density of the serum is consequently greater than usual; its colour is remarkably black even in the arteries; in some cases it is semi-fluid and incapable of coagulating, having the appearance of tar; and the salts of the blood are often in unusually small quantity, being sometimes almost entirely wanting. On comparing the condition of the blood with that of the discharges, it is manifest that the latter contain all the ingredients of the blood except the red globules; but that the aqueous and saline parts pass out of the circulation more rapidly than the albuminous.

The cause of the dark colour of the blood in cholera is a point by no means decided. Dr. Thomson states that the blood in cholera is not rendered florid by exposure to atmospheric air, and hence argues that the dark colour is owing to some diseased condition of the blood which unfits it for being duly arterialized; but this view is opposed to the statement of Dr. O'Shaughnessy, who declares that the dark blood in cholera is susceptible of arterialization,—that, at least, on being agitated with air, it is rendered florid, absorbs oxygen, and emits carbonic acid gas. Dr. Stevens, in his treatise on the blood, maintains that the black colour is primarily owing to the contagion of cholera, which throws the circulating fluids into a morbid state; and that the effect of the poison is increased by the diminished quantity of saline matter, an opinion intimately connected with his theory of arterialization, which will shortly be explained. He has observed the blood of persons living in a cholera hospital to be preternaturally dark, though they were not affected with the disease. Perhaps the most correct opinion is, that the blood of persons in cholera, in consequence of deranged arterial action, circulates sluggishly, and is hence imperfectly arterialized: from this cause the dark colour may arise without any diminution of saline matter; and it may disappear, from an improved circulation, without the administration of salt. But there is no doubt that loss of saline matter increases the dark tint of the blood, and prevents it from acquiring the arterial colour.

The substance known under the name of *black vomit*, ejected by the stomach during the last stage of yellow fever, appears from the observations of Dr. Stevens to be blood blackened and partially coagulated by a free acid. The acidity is suspected by Dr. Prout to arise from the secretion of acetic acid; and the presence of hydrochloric acid is also probable.

Respiration.

When venous blood is brought into contact with atmospheric air, its surface passes from a dark purple to a florid-red colour, oxygen gas disappears, and carbonic acid gas is emitted. The change takes place more speedily when air is agitated with blood; it is still more rapid when pure oxygen is substituted for atmospheric air; and it does not occur at all when oxygen is entirely excluded. These facts, which were long considered indisputable, have been questioned by Dr. Davy; but they are nevertheless perfectly true, and have been fully established by Dr. Christison. (Edin. Med. and Surg. Journal, Jan. 1831.) The quantity of carbonic acid developed very exactly corresponds with the oxygen which disappears; but when the blood and air are agitated together, part of the carbonic acid which would otherwise be found as gas, is absorbed by the serum. It appears certain, from the experiments of Dr. Christison, that the colouring matter is the part of the blood essentially concerned in the phenomenon; an inference which is drawn, not from the mere change of tint, but from the effect of the blood on the air varying with the quantity and condition of the colouring matter. In some fevers, as acute rheumatism, in which the circulation is rapid and the respiration free, the venous blood is found to be very florid, and to withdraw very little oxygen from air; and a similar scanty abstraction of oxygen is observed in dark venous blood, when its usual proportion of colouring matter is deficient.

The conversion of the dark purple colour of venous blood into the florid tint of that contained in the arteries, is familiarly expressed by the term *arterialization;* or, more strictly, this name is applied to a change in the constitution of the blood, which is accompanied and indicated by change of colour, evolution of carbonic acid, and abstraction of oxygen from the air.

Chemists have differed about the origin of the carbonic acid. Some suppose that the blood, in circulating through the body, becomes charged with carbon in some unknown mode of combination, which causes the venous character; and that when such blood is exposed to the air, its redundant carbon, by a process of oxidation, unites directly with atmospheric oxygen, the carbonic acid so generated is set free, and the blood unloaded of carbon recovers the arterial character. By others, venous blood is thought to owe its colour to the presence of carbonic acid ready formed within it: they maintain that oxygen gas is directly absorbed into the blood, and displaces the pre-existing carbonic acid. The near coincidence between the quantity of evolved carbonic acid and absorbed oxygen, which has been urged in favour of the former theory, is scarcely an argument either way; for though true, on the one hand, that carbonic acid contains its own volume of oxygen, it is also true, on the other, that if one gas displaces another from a liquid, the volumes of evolved and absorbed gas usually correspond. The strongest evidence is in favour of the latter theory. Carbonic acid has been proved to be capable when absorbed by arterial blood of causing the venous character; and Mr. Hoffman has shown that when venous blood is received from a vein into a vessel full of hydrogen gas, without exposure to the atmosphere, and is then agitated with the hydrogen, carbonic acid gas is evolved. (Medical Gazette, March 30, 1833.)

But arterialization does not alone depend, as was thought till lately, on the influence of the atmosphere. Dr. Stevens, in his treatise on the blood, h the merit of proving the saline matter of the serum to be essential to phenomenon. Various salts, such as nitre, chlorate of potassa, sea-salt, and bicarbonate of soda, have the property of giving to hematosine, or the colouring principle of the blood, a bright red tint, far more florid, when a strong saline solution is used, than arterial blood. A saline solution of the requisite strength gives to venous blood the arterial tint, without exposure to the air; but the serum contains so small a quantity of salt that its effect becomes visible only when aided by the agency of the atmosphere. A clot of venous blood, when carefully separated from its serum, is not brightened by oxygen gas; and arterial blood, when its serum is displaced by pure water, becomes as dark as venous blood. Hence it may be inferred that the change from venous to arterial blood consists of two parts which are essentially distinct: one is attended with the direct absorption of oxygen, and the evolution of carbonic acid pre-existing in venous blood, an action essential to life; and the other, the most conspicuous but probably least essential, is the effect of the saline parts of the serum, which impart a florid tint to the colouring matter after the former change has occurred. By what means the absorption of oxygen gives rise to the evolution of carbonic acid, is a question which, like others that will occur to the attentive reader, has not been sufficiently explained, and invites further investigation.

The same changes which occur in blood out of the body are continually taking place within it. During respiration, venous blood is exposed in the lungs to the agency of the air and is arterialized, oxygen gas disappears, and carbonic acid is evolved; and it is remarkable that these phenomena ensue not only during life, but even after death, provided the respiratory process be preserved artificially. Since, therefore, all the characteristic phenomena of arterialization are the same in a living and in a dead animal, and whether the blood is or is not contained in the body, it seems legitimate to infer, that this process is not necessarily dependent on the vital principle, but is solely determined by the laws of chemical action.

In studying the subject of respiration, the first object is to determine the precise change produced in the constitution of the air which is inhaled. Dr. Black was the first to notice that the air exhaled from the lungs contains a considerable quantity of carbonic acid, which may be detected by transmission through lime-water. Priestley, some years after, observed that air is rendered unfit for supporting flame or animal life by the process of respiration; from which it was probable that oxygen is consumed; and Lavoisier subsequently established the fact, that during respiration oxygen gas disappears, and carbonic acid is disengaged. The chief experimentalists who have since cultivated this department of chemical physiology are, Priestley, Scheele, Lavoisier, Seguin, Crawford, Goodwin, Davy, Ellis, Allen and Pepys, Edwards, and Despretz. Of these, the results obtained by Messrs. Allen and Pepys (Phil. Trans. 1808), and Dr. Edwards,* are the most conclusive and satisfactory; their researches having been conducted with great care, and aided by all the resources of modern chemistry.

One of the chief objects of Allen and Pepys, in their experiments, was to ascertain if any uniform relation exists between the oxygen consumed and the carbonic acid evolved. They found in general that the quantity of the former exceeds that of the latter; but as the difference was very trifling, they inferred that the carbonic acid of the expired air is exactly equal to the oxygen which disappears. The experiments of Dr. Edwards were attended with a remarkable result, which accounts very happily for some of the discordant statements of preceding inquirers. He found the ratio between the gases to vary with the animal. In some animals it might be regarded as nearly equal; while in others the loss of oxygen considerably exceeded the gain of carbonic acid, so that the respired air suffered a material diminution in volume. With respect to the human subject, the statement of Allen and Pepys seems very near the truth.

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* De l'Influence des Agens Physiques sur la Vie, 1824.

The quantity of oxygen withdrawn from the atmosphere, and of carbonic acid disengaged, is variable in different individuals, and in the same individual at different times. It is estimated by Allen and Pepys, that in every minute during the calm respiration of a healthy man of ordinary stature, 26.6 cubic inches of carbonic acid of the temperature of 50° are emitted, and an equal volume of oxygen withdrawn from the atmosphere. From these data it has been calculated, that in an interval of twenty-four hours not less than eleven ounces of carbon are given off from the lungs alone,—an estimate which must surely be inaccurate, the quantity being so great as sometimes to exceed the weight of carbon contained in the food. The same observers have lately found the production of carbonic acid in a pigeon, breathing freely in atmospheric air, to be such that, supposing the same rate to continue, the bird must have thrown off 96 grains of carbon in the space of 24 hours. From the observations of Dr. Prout, it appears that the quantity of carbonic acid emitted from the lungs is variable at particular periods of the day, and in particular states of the system. It is more abundant during the day than the night; about daybreak it begins to increase, continues to do so till about noon, and then decreases until sunset. During the night it seems to remain uniformly at a minimum; and the maximum quantity given off at noon exceeds the minimum by about one-fifth of the whole. The quantity of carbonic acid is diminished by any debilitating causes, such as low diet, depressing passions, and the like. (An. of Phil. xiii. 269.) The experiments of Dr. Fyfe, published in his Inaugural Dissertation, are confirmatory of those above mentioned.

Messrs. Allen and Pepys observed that atmospheric air, when drawn into the lungs, returns charged in the succeeding expiration with from 8 to 6 per cent. of carbonic acid gas; but this estimate is probably too high, since in some recent observations of Dr. Apjohn of Dublin, air, once respired, contained only 3.6 per cent. of carbonic acid. When an animal is confined in the same quantity of air, death ensues before all the oxygen is consumed: when the same portion of air is repeatedly respired until it can no longer support life, it then contains 10 per cent. of carbonic acid according to Allen and Pepys, and barely 8 per cent. according to Dr. Apjohn. (Edin. Med. and Surg. Journal, Jan. 1831.)

Although in respiration the arterialization of the blood by means of free oxygen is the essential change, without the due performance of which the life of warm-blooded animals cannot be preserved beyond a few minutes, and which is likewise necessary to the lowest of the insect tribe, it is important to determine whether the nitrogen of the atmosphere has any influence in the function. The results of different inquirers differ considerably. In the experiments of Priestley, Davy, Humboldt, Henderson, and Pfaff, there appeared to be absorption of nitrogen, a less quantity of that gas being exhaled than was inspired. Nysten, Berthollet, and Despretz, on the contrary, remarked an increase in the bulk of the nitrogen; and from the researches of Seguin and Lavoisier, Vauquelin, Ellis, Dalton, and Spallanzani, it was inferred that there is neither absorption nor exhalation of nitrogen, the quantity of that gas undergoing no change during its passage through the air-cells of the lungs. Allen and Pepys arrived at a similar conclusion; and since the appearance of their Essay, the opinion has prevailed very generally among physiologists, that in respiration the nitrogen of the air is altogether passive.

The facts ascertained by Edwards relative to this subject are novel and of peculiar interest. This acute physiologist has reconciled the discordant results of preceding experimenters by showing that, during the respiration even of the same animal, the quantity of nitrogen may one while be increased, at another time diminished, and at a third wholly unchanged. He has traced these phenomena to the influence of the seasons; and he suspects, as indeed is most probable, that other causes, independently of season, have a share in their production. In nearly all the lower animals which were made the subject of experiment, an augmentation of nitrogen was observable during summer. Sometimes, indeed, it was so slight that it might be disregarded. But in many other instances, it was so great as to place the fact beyond the possibility of doubt; and on some occasions it almost equalled the whole bulk of the animal. Such continued to be the result of his inquiries until the close of October, when he observed a sensible diminution of nitrogen, and the same continued throughout the whole of winter and the beginning of spring.

There are two modes of accounting for these phenomena. According to one view, the nitrogen which disappears is ascribed to the absorption of what was inhaled, and its increase to direct exhalation, the opposite processes of absorption and exhalation being supposed not to occur at the same moment. According to the other view, both these processes are always going on at the same time, and the result depends on the preponderance of one over the other. When absorption prevails, a smaller quantity of nitrogen is exhaled than was inspired; when exhalation exceeds absorption, increase of nitrogen takes place; but when absorption and exhalation are equal, the bulk of the inspired air, so far as concerns nitrogen, is unchanged. The latter opinion, which is adopted by Edwards, is supported by two decisive experiments performed by Allen and Pepys, in one of which a guinea-pig was confined in a vessel of oxygen gas, and in the other in an atmospere composed of 21 measures of oxygen and 79 of hydrogen. In both cases the residual air contained a quantity of nitrogen greater than the bulk of the animal itself; and in the latter a portion of hydrogen had disappeared. Hence it follows that nitrogen may be exhaled from the lungs, and that hydrogen may be absorbed.

An account of some interesting researches on the respiration of birds, bearing directly on this subject, was published in 1829 by Allen and Pepys. (Phil. Trans.) The subject of inquiry was the pigeon, and the phenomena attending its respiration were observed under three different circumstances, namely, in atmospheric air, in oxygen gas, and in a mixture of oxygen and hydrogen, in which the former amounted, as in the atmosphere, to 20 per cent. In each case the bulk of the gaseous mixture remained without change. In the experiments with atmospheric air, the oxygen which disappeared was equal to the carbonic acid evolved; the nitrogen was unaffected, except on one occasion when the bird appeared uneasy, and then there was a slight loss of nitrogen. In oxygen gas the production of carbonic acid was about half the quantity emitted when the pigeon breathed common air; and the decrease in oxygen was exactly equal to the united volumes of the carbonic acid and nitrogen which were disengaged. When the pigeon was placed in mixed oxygen and hydrogen gases, the production of carbonic acid was rather more abundant than in atmospheric air, and its volume equalled exactly the loss in oxygen; nitrogen, as before, was given out with considerable freedom, and its bulk precisely corresponded to the decrease in hydrogen. In the two latter series of experiments, especially in the last, the respiration of the pigeon was at times laborious. The experiments, however, are decisive of the fact, that carbonic acid and nitrogen gases may be thrown off from the lungs, and that oxygen and hydrogen gases may be absorbed.

Two theories similar to those of arterialization (page 609) have been proposed to explain the phenomena of respiration. According to one theory, the carbonic acid found in the respired air is actually generated in the lungs themselves; while, according to the other, this gas is thought to exist ready formed in the blood, and to be merely thrown off from that liquid during its distribution through the lungs. The former theory, which appears to have originated with Priestley, has received several modifications. Priestley imagined that the phenomena of respiration are owing to the disengagement of phlogiston from the blood, and its combination with the air. Dr. Crawford modified this doctrine in the following manner. (Crawford on Animal Heat.) He was of opinion that venous blood contains a peculiar compound of carbon and hydrogen, termed *hydro-carbon*, the elements of which unite in the lungs with the oxygen of the air, forming water with the one, and carbonic acid with the other; and that the blood, thus purified, regains its florid hue, and becomes fit for the purposes of the animal economy.

The hypothesis of Crawford, however, is not merely liable to the objection that the supposed hydro-carbon, as respects the blood, is quite imaginary; but it was found at variance with the leading facts established by Allen and Pepys. By the elaborate researches of these chemists it was established, that carbonic acid gas contains its own volume of oxygen; and they also concluded that air, inhaled into the lungs, returns charged with a quantity of carbonic acid, almost exactly equal in bulk to the oxygen which disappears—an inference which, as applied to man and some of the lower animals, seems very near the truth. A review of these circumstances induced them to adopt the opinion, that the oxygen of the air combines in the lungs exclusively with carbon; and that the watery vapour, which is always contained in the breath, is an exhalation from minute pulmonary vessels. They conceived that the fine animal membrane interposed between the blood and the air does not prevent chemical action from taking place between them.

This view has been further modified by Mr. Ellis, who supposes that the carbon is separated from the venous blood by a process of secretion, and that then, coming into direct contact with oxygen, it is converted into carbonic acid. (Inquiry, &c. Parts i. and ii.) The circumstance which led Mr. Ellis to this opinion, was a disbelief in the possibility of oxygen acting upon the blood through the animal membrane in which it is confined. This difficulty, as will immediately appear, no longer exists; and the free permeability of membranes by gases is now completely established.

According to the second theory, which was supported by Le Grange and Hassenfratz, and has lately been adopted by Edwards, carbonic acid generated during the course of the circulation is given off from venous blood in the lungs, and oxygen gas is absorbed. This doctrine, though generally regarded hitherto as less probable than the preceding, is supported by very powerful arguments. The experiments and observations of Dr. Edwards seem to leave no doubt that the blood, while circulating through the lungs, is capable of absorbing hydrogen, nitrogen, and oxygen gases, and of emitting nitrogen; and he has gone very far towards proving that the carbonic acid is derived from the same source. On confining frogs and snails for some time in an atmosphere of hydrogen, the residual air was found to contain a quantity of carbonic acid, which was in some instances even greater than the bulk of the animal; and a similar result was obtained with young kittens.

These facts, in proving the possibility of gaseous inhalation and exhalation, as well as the evolution of carbonic acid independently of atmospheric air, entitle the theory of Edwards to a preference; and they will go far, when attested by more extensive observation, especially should the constant presence of carbonic acid in venous blood be established, to the rejection of the former theory.

The difficulty which formerly stood in the way of both theories of respiration, arising from the supposed impermeability of animal membranes by gases, has been entirely removed by the researches of Drs. Faust and Mitchell. (American Journal of the Medical Sciences, No. 13.) It fully appears from their experiments, and of the accuracy of their principal results I am satisfied from personal observation, that animal membranes both in the living and dead subject, both in and out of the body, are freely penetrable by gaseous matter;—that the phenomena of endosmose and exosmose, observed in liquids by Dutrochet, are likewise exhibited by gases. If a glass full of carbonic acid be closed by an animal membrane, such as the cœcum of a fowl, or the bladder of a sheep, and be then exposed to the atmosphere, a portion of air will pass into the glass and some of the confined gas escape from it; and if the experiment be reversed by confining air in the glass, which is then placed in an atmosphere of carbonic acid, the latter passes in and the former out of the glass. Similar phenomena ensue with other gases; so that when any two gases are separated by a membrane, both of them pass through the partition. The permeability of a membrane is greater in a living than in a dead animal; but the property is by no means peculiar to organized matter, since a thin lamina of any substance of organic origin, such as a sheet of caoutchouc, is freely permeable. Water and other liquids transmit gases apparently on the same principle as membranes; and porous solid bodies of the mineral kingdom will doubtless be found to possess a similar property.

But though all gases pass through membranous septa, they differ remarkably in the relative rapidity of transmission. Thus Dr. Mitchell found that the time required for the passage of equal volumes of different gases through the same membrane, was 1 minute with ammonia, 2½ minutes with sulphuretted hydrogen, 3¼ with cyanogen, 5½ with carbonic acid, 6½ with protoxide of nitrogen, 27½ with arseniuretted hydrogen, 28 with olefiant gas, 37½ with hydrogen, 113 with oxygen, 160 with carbonic oxide, and a much greater time with nitrogen. Hence, when a bladder full of air is surrounded with carbonic acid, the latter enters faster than the former escapes, and the bladder bursts; but on reversing the conditions of the experiment, the bladder becomes flaccid, because the carbonic acid within passes out more rapidly than the exterior air enters. The transmission of gases in some of these experiments takes place in opposition to a pressure equal to several atmospheres.

It would perhaps be premature to speculate on the cause of this singular property of gases, nor is it material for my present purpose to do so; but as the reader will naturally desire some explanation, the following, which is nearly that of Dr. Mitchell, may be given as most consistent with the known properties of matter.—The passage of a gas through a membrane or other substance containing within it very fine pores, appears to depend in the first place on the power of the porous body to absorb the gas into its substance. This action is apparently of the same kind as that exerted on gases by charcoal, and seems to depend on the attraction which all bodies similar or dissimilar exert upon each other, such as is exemplified by the tendency of contiguous floating bodies to approach one another, by the adhesion of water to the surface of glass, and the ascent of liquids in capillary tubes. The absorbent power of such bodies, which may thus be regarded as aggregates of capillary tubes, will vary with the size and number of the pores. The entrance of a gas into such pores will be promoted by its elasticity; but the same force will oppose its retention within the pores, will resist its return into the mass of the same particles, and urge it to escape where there is no such resistance. Hence, when two gases are separated by a membrane, each passes through, and mixes with the other: the penetration of each is arrested as soon as its individual elasticity is the same on both sides of the partition, and therefore that gas which penetrates the membrane the more rapidly, is the first to be stationary. The relative velocity of transmission is doubtless a complex phenomenon, referable to the natural elasticity of each gas, to its diffusiveness, to its affinity for water, and to the size of its atom should that differ in different gases. The power of different liquids to absorb gases with which they have no chemical action, is explicable on the same principles. A gas may be absorbed by such a liquid, entering between its particles as into the pores of a membrane: on exposure to a different atmosphere, a portion of the absorbed gas escapes, and about an equal volume of the other enters the space which the former had occupied. But whatever may be thought of these speculations, the facts which they are designed to explain are obviously applicable to the phenomena of respiration. It is clear that oxygen has free ingress to the blood through the fine membrane of the lungs; and carbonic acid, whether pre-existing in venous blood or generated during its flow through the lungs, has a free passage outwards. This is a sufficiently direct inference from what has already been mentioned; but it may be added, as additional evidence, that an aqueous solution of carbonic acid confined in a bladder gives out that gas to the surrounding atmosphere, and that venous blood exposed in a bladder to the air, absorbs oxygen, emits carbonic acid, and acquires the arterial character.

It appears from the essays of Drs. Faust and Mitchell that their attention was awakened to the permeability of membranes to gases by the endosmose and exosmose of liquids described by Dutrochet, by an insulated example of a similar phenomenon in gases observed by Mr. Graham, and by some facts of a like kind noticed long ago by Priestley. Dr. Stevens also, as stated at page 96 of his treatise on the blood, was aware that carbonic acid passes readily through animal membranes when air is on the other side, applied that fact to the theory of respiration, and brought the subject under the notice of several men of science in New York shortly before the publication of Drs. Faust and Mitchell. But the views of Dr. Stevens, though well calculated to elicit inquiry, were vague and partial; and the American philosophers are entitled to the merit of advancing from the detached facts of others to the establishment of a principle.

The conversion of venous into arterial blood appears not to be confined to the lungs. The disengagement of carbonic acid from the surface of the skin, and the corresponding disappearance of oxygen gas, was demonstrated by the experiments of Jurine and Abernethy; and although the accuracy of their results has been doubted by some persons, it has been confirmed by others. However this may be in the human subject, the fact with respect to many of the lower animals is unquestionable. Spallanzani proved that some animals possessed of lungs, such as serpents, lizards, and frogs, produce the same changes on the air by means of their skin, as by their proper respiratory organs; and Dr. Edwards, in a series of masterly experiments, has shown that this function compensates so fully for the want of respiration by the lungs, as to enable these animals, in the winter season, to live for an almost unlimited period under the surface of water.

Animal Heat.

The striking analogy between the processes of combustion and respiration, in both of which oxygen gas disappears, and an oxidized body is substituted for it, led Dr. Black to infer that the heat generated in the animal system, by means of which the more perfect animals preserve their temperature above that of the surrounding medium, is derived from the changes going forward in the lungs. But this opinion is not founded on analogy alone; many circumstances conspire to show that the developement of animal heat is dependent on the function of respiration, although the mode by which the effect is produced has not hitherto been satisfactorily determined. Thus, in all animals whose respiratory organs are small and imperfect, and which, therefore, consume but a comparatively minute quantity of oxygen, and generate little carbonic acid, the temperature of the blood varies with that of the medium in which they live. In warm-blooded animals, on the contrary, in which the respiratory apparatus is larger, and the chemical changes more complicated, the temperature is almost uniform; and those have the highest temperature whose lungs, in proportion to the size of their bodies, are largest, and which consume the greatest quantity of oxygen. The temperature of the same animal at different times is connected with the state of the respiration. When the blood circulates sluggishly, and the temperature is low, the quantity of oxygen consumed is comparatively small; but, on the contrary, a large quantity of that gas disappears when the circulation is brisk, and the power of generating heat energetic. It has also been observed, especially by Crawford and De Laroche, that when an animal is placed in a very warm atmosphere, so as to require little heat to be generated within his own body, the consumption of oxygen is unusually small, and the blood within the veins retains the arterial character.

The connexion between the power of generating heat and respiration has been illustrated in a very pointed manner by Dr. Edwards. Some young animals, such as puppies and kittens, require so small a quantity of oxygen for supporting life, that they may be deprived of that gas altogether for twenty minutes without material injury; and it is remarkable that so long as they possess this property, the temperature of their bodies sinks rapidly by free exposure to the air. But as they grow older they become able to maintain their own temperature, and at the same time their power to endure the privation of oxygen ceases. The same observation applies to young sparrows, and other birds which are naked when hatched; while young partridges, which are both fledged and able to retain their own temperature at the period of quitting the shell, die when deprived of oxygen as rapidly as an adult bird.

The first consistent theory of the production of animal heat was proposed by Dr. Crawford. This theory was founded on the assumption that the carbonic acid contained in the breath is generated in the lungs, and that its formation is accompanied with disengagement of caloric. But since the temperature of the lungs is not higher than that of other internal organs, and arterial very little if at all warmer than venous blood, it follows that the greater part of the caloric, instead of becoming free, must in some way or other be rendered insensible. Accordingly, on comparing the specific caloric of arterial and venous blood, Dr. Crawford found the capacity of the former to exceed that of the latter in the ratio of 1030 to 892. He, therefore, inferred that the dark blood within the veins, at the moment of being arterialized, acquires an increase of insensible caloric; and that while circulating through the body, and gradually resuming the venous character, it suffers a diminution of capacity, and evolves a proportional degree of heat.

Unfortunately for the hypothesis of Crawford, one of the leading facts on which it is founded has been called in question; Dr. Davy maintaining, on the authority of his own experiments, that there is little or no difference between the capacity of venous and arterial blood. (Philos. Trans. for 1814.) If this be true, the hypothesis itself necessarily falls to the ground. One part of the doctrine of Crawford may, however, in a modified form, be applied to the theory of respiration advocated by Dr. Edwards. For if oxygen be absorbed by the blood in its passage through the lungs, and carbonic acid, ready formed, be emitted in return, it follows that this gas must be generated during the course of the circulation; and it may be inferred that the heat developed in consequence of this chemical change is at once communicated to the adjacent organs. In this way the question concerning the capacity of the blood for caloric may be entirely disregarded.

While some physiologists have been disposed to refer the source of animal heat entirely to the alternate changes of venous to arterial, and of arterial to venous blood, others have denied its agency altogether, ascribing the evolution of caloric solely to the influence of the nervous system. The chief foundation for this opinion is in the experiments of Mr. Brodie, who inflated the lungs of animals recently killed by narcotic poisons or division of the spinal marrow. (Phil. Trans. for 1811 and 1812.) In an animal so treated, the blood continued to circulate, oxygen gas disappeared, carbonic acid was evolved, and the usual changes of colour took place with regularity; but notwithstanding the concurrence of all these circumstances, the temperature fell with equal if not greater rapidity than in another animal killed at the same time, but in which artificial respiration was not performed.

Were these experiments rigidly exact, they would lead to the opinion that no caloric is evolved by the mere process of arterialization. This inference, however, cannot be admitted for two reasons:—first, because other physiologists, in repeating the experiments of Brodie, have found that the process of cooling is retarded by artificial respiration; and, secondly, because it is difficult to conceive why the formation of carbonic acid, which uniformly gives rise to increase of temperature in other cases, should not be attended within the animal body with a similar effect. It may hence be inferred, that this is one of the sources of animal heat. It is certain, however ,that the heat of animals cannot be maintained by the sole process of arterialization. sistently with this fact, the researches of Dulong and Despretz agree in ing, in opposition to the results obtained by Lavoisier and Crawford, healthy animal imparts to surrounding bodies a quantity of heat cons bly greater than can be accounted for by the combustion of the c thrown off during the same interval from the lungs in the form of ca acid. (An. de Ch. et de Ph. xxvi.)

Though the influence of the nervous system over the developem animal heat is no longer doubtful, physiologists are not agreed as mode by which it operates. Its action may either be direct or indirect is, the nerves may possess some specific power of generating heat, o may excite certain operations by which the same effect is occasioned. far from improbable, that the nerves act more by the latter than the f mode; that the infinite number of chemical phenomena going on in t nute arterial branches during the processes of secretion and nutritio cesses which are entirely dependent on the nervous system, are at with disengagement of caloric. This view has, at least, been ably de by Dr. Williams in an essay published in the Medico-Chir. Trans. of burgh. (Vol. ii.)

SECTION II.

SECRETED FLUIDS SUBSERVIENT TO DIGESTION.

Saliva.

The saliva is a slightly viscid liquor, secreted by the salivary When mixed with distilled water, a flaky matter subsides, which is derived apparently from the lining membrane of the mouth. The cl lution, when exposed to the agency of galvanism, yields a coagulum, hence inferred by Mr. Brande to contain albumen; but the quantity principle is so very small that its presence cannot be demonstrated other reagent. The greater part of the animal matter remaining liquid is peculiar to the saliva, and may be termed *salivary matter*. soluble in water, insoluble in alcohol, and, when freed from the accom ing salts, is not precipitated by subacetate of lead, corrosive sublim infusion of gall-nuts. The saliva likewise contains a small quantity mal matter, which is soluble both in alcohol and water, and which posed by Tiedemann and Gmelin to be osmazome.

The solid contents of the saliva, according to Berzelius, do not seven in 1000 parts, the rest being water. From the analysis of Tied and Gmelin, the chief saline constituent is chloride of potassium; bu ral other salts, such as the sulphate, phosphate, acetate, and carbo potassa, are likewise present in small quantity. The saliva of the subject, according to the same authority, contains very little soda. T perty which the saliva possesses of striking a red colour with a pe iron is owing to sulpho-cyanuret of potassium. This salt exists also saliva of the sheep; but it has not been found in that of the dog. T liva of the sheep contains so much carbonate of soda, that it effe with acids.

The only known use of the saliva is to form a soft pulpy mass w food during mastication, so as to reduce it into a state fit for bein lowed with facility, and for being more readily acted on by the juice stomach.

Concretions are sometimes found in the salivary glands and ducts. contained in the salivary gland of an ass was found by M. Caventou tain 91.6 parts of carbonate of lime, 4.8 of phosphate of lime, and 3.6 of animal matter. A salivary concretion of a horse was found by M. Henry, jun. to consist of carbonate of lime 85.52, carbonate of magnesia 7.56, phosphate of lime 4.40, and 2.48 of animal matter. Carbonate of lime is the chief ingredient of salivary concretions.

Pancreatic Juice.

This fluid is commonly supposed to be analogous to the saliva, but it appears from the analys is of Tiedemann and Gmelin that it is essentially different. The chief animal matters are albumen, and a substance like curd; but it also contains a small quantity of salivary matter and osmazome. It reddens litmus paper, owing to the presence of free acid, which is supposed to be the acetic. Its salts are nearly the same as those contained in the saliva, except that sulphocyanic acid is wanting. The uses of this fluid are entirely unknown.

Gastric Juice.

The gastric juice, collected from the stomach of an animal killed while fasting, is a transparent fluid which has a saline taste, and has neither an acid nor alkaline reaction. During the process of digestion, on the contrary, it is found to be distinctly acid. Thus free hydrochloric acid was detected under these circumstances by Dr. Prout in the stomach of the rabbit, hare, horse, calf, and dog (Phil. Trans. 1824); and he has discovered the same acid in the sour matter ejected from the stomach of persons labouring under indigestion, a fact which has since been confirmed by Mr. Children. Tiedemann and Gmelin observed that the secretion of acid commences as soon as the stomach receives the stimulus of food or any foreign body. This effect is occasioned, for example, by the presence of flint stones or other indigestible matters; but it is produced in a still greater degree by substances of a stimulating nature. According to their observation the acidity is owing to the secretion of free hydrochloric and acetic acids.

The gastric juice coagulates milk, apparently in consequence of the acid secreted during digestion. According to the experiments of Spallanzani and Stevens it is highly antiseptic, not only preventing putrefaction, but rendering meat fresh after it is tainted. But of all the properties of the gastric juice, its solvent virtue is the most remarkable, being that on which depends the first stage of the process of digestion. When the food is introduced into the stomach, it is there intimately mixed with the gastric juice, by the agency of which it is dissolved, and converted into a semifluid matter called *chyme*. That this change is really owing to the solvent power of the gastric juice fully appears from the researches of Spallanzani, Reaumur, and Stevens. In the experiments of Dr. Stevens, described in his Inaugural Dissertation, the common articles of food were enclosed in hollow silver spheres perforated with holes, and after remaining for some time within the stomach, completely protected from pressure and trituration, the alimentary substances were found to have been entirely dissolved. A similar effect takes place when nutritious matters, out of the body, are mixed with the gastric fluid, and the mixture is exposed to a temperature of 100°. So great, indeed, is the solvent power of this fluid, that it has been known to dissolve the coats of the stomach itself; at least the corrosions of this organ sometimes witnessed in persons who have died suddenly while fasting, and in good health, were ascribed by the celebrated physiologist, John Hunter, to this cause. That the agent here assigned is adequate to produce such an effect, has been fully proved by my colleague, Dr. Carswell. (Edin. Med. and Surg. Journal, October, 1830.) Rabbits were killed by a blow on the head during digestion, and then suspended for some hours by the hinder legs. The most dependent parts of the stomach, to which the fluids had gravitated, were invariably more or less dissolved: in some cases the textures were thin, white, soft, and pulpy; and in others, complete perforations existed, and the contiguous viscera were attacked. The blood in the vessels of the corroded part was black and more or less coagulated, an effect analogous to that produced by an acid. The corroding fluid, as during healthy digestion, was strongly acid; and this acid liquor, taken from the stomach of one rabbit and introduced into that of another previously killed, produced corrosion.

Great diversity of opinion has prevailed respecting the cause of the solvent property of the gastric fluid. It was formerly ascribed to some specific power, and was thought to be inexplicable on any known chemical principles; but the more precise observation of recent experimentalists has removed one great part of the mystery. Tiedemann and Gmelin directly ascribe the solvent action of the gastric juice to the acid which it contains: they found healthy digestion to be invariably attended with the secretion of hydrochloric and acetic acids, and ascertained that these acids, at the temperature of the body, are capable of dissolving all the digestible substances employed as food. Similar remarks on the invariable connexion between the acidity and solvent power of the gastric fluids have been made by Dr. Carswell, who informs me of the additional decisive fact, that on neutralizing the gastric juice with magnesia, its solvent property was destroyed. It would thus seem that the stimulus of food causes the neutral salts of the blood circulating in the stomach to be decomposed, either by a purely vital process, or, as Dr. Prout suggests, by a galvanic operation (Bridgewater Treatise); that the alkali remains in the blood, causing the alkalinity of that liquid; and that the acids, passing into the stomach, dissolve the food.

Bile.

The bile is a yellow or greenish-yellow coloured fluid, of a peculiar sickening odour, and of a taste at first sweet and then bitter, but exceedingly nauseous. Its consistence is variable, being sometimes limpid, but more commonly viscid and ropy. It is rather denser than water, and may be mixed with that liquid in every proportion. It contains a minute quantity of free soda, and is, therefore, slightly alkaline; but owing to the colour of the bile itself, its action on test paper is scarcely visible.

Of the chemists who have of late years investigated the composition of the bile, Thenard, Berzelius, Tiedemann, and Gmelin deserve particular mention. In an elaborate essay published in the *Memoires d'Arcueil*, vol. i. Thenard endeavoured to show that the bile of the ox consists of three distinct animal principles, a yellow colouring matter, a species of resin, and a peculiar substance, to which, from its sweetish bitter taste, he applied the name of *picromel*. According to his analysis, 800 parts of bile consist of water 700 parts, resin 15, picromel 69, yellow matter about 4, soda 4, phosphate of soda 2, muriates of soda and potassa 3.5, sulphate of soda 0.8, phosphate of lime and perhaps magnesia 1.2, and a trace of oxide of iron. He supposed the resin to be combined with the picromel and soda, and ascribes its solubility in water to this cause.

Berzelius takes a totally different view of the constitution of the bile. He denies that this fluid contains any resinous principle, and regards the yellow matter, resin, and picromel of Thenard, as one and the same substance, to which he applies the name of *biliary matter*. (Medico-Chir. Trans. iii.) Tiedemann and Gmelin, however, in their recent work on Digestion, admit the existence of picromel and resin as the chief constituents of bile; although it appears from their experiments that the substance described by Thenard as picromel was not pure, but contained a portion of resin. According to the analysis of these chemists, the bile of the ox is a very complex fluid, consisting of the following ingredients:—water to the extent of 91.5 per cent.; a volatile odoriferous principle; cholesterine; resin; asparagin; picromel; yellow colouring matter; a peculiar azotized substance soluble in water and alcohol; a substance which is soluble in hot alcohol, but insoluble in water, supposed to be gluten; osmazome; a principle which emits a urinous odour when heated; a substance analogous to albumen or caseous matter; and mucus. The salts of the bile are the margarate, oleate, acetate, *cholate*, bicarbonate, phosphate, sulphate, and hydrochlorate of soda, together with a little phosphate of lime. The *cholic* is a peculiar animal acid, which crystallizes in needles, reddens litmus paper, and is distinguished from analogous compounds by having a sweet taste.

The flaky precipitate which is occasioned by adding acids to bile from the ox, consists of several substances. At first the caseous and colouring matters, along with mucus, are thrown down; and, afterwards, the margaric acid and a compound of picromel and resin with the acid employed are precipitated. When acetate of lead is mixed with this fluid, a white precipitate falls, which consists of oxide of lead combined with the phosphoric, sulphuric, and several other acids, together with a small quantity of the compound of picromel and resin. On adding subacetate of lead to the clear liquid, a copious precipitate ensues, consisting chiefly of picromel, resin, and oxide of lead. If this compound be suspended in water, through which a current of hydrosulphuric acid gas is transmitted, sulphuret of lead and the resin subside, while the picromel remains in solution. By collecting and drying the precipitate, and digesting it in alcohol, the resin is dissolved, and may be obtained by evaporation. The aqueous solution, when evaporated, yields the picromel of Thenard; but according to Tiedemann and Gmelin, it still contains a portion of resin. The chief difficulty, indeed, of preparing pure picromel arises from its tendency to dissolve the resin; and the only mode of separation is by throwing them down repeatedly by means of subacetate of lead. By this process the affinity of the picromel and resin for each other is gradually lessened, until at length the separation is rendered complete.

Pure picromel occurs in opaque, rounded, crystalline particles, is soluble in water and alcohol, but is insoluble in ether. Its taste is sweet without any bitterness; but it cannot be regarded as a species of sugar, because a large quantity of nitrogen enters into its composition. Its aqueous solution is not precipitated by acids, nor by acetate and subacetate of lead. When digested with the resin of bile, a portion of the latter is dissolved, and a solution is obtained, which has both a bitter and sweet taste, and yields a precipitate with subacetate of lead and the stronger acids. This is the compound which causes the peculiar taste of the bile.

The bile of the human subject has not been studied so minutely as that of the ox. According to Thenard it consists, besides salts, of water, colouring matter, albumen, and a species of resin. Chevallier has since detected picromel, and Chevreul cholesterine, in human bile; and both these discoveries have been confirmed by the observations of Tiedemann and Gmelin.

The derangement which takes place in the system when the secretion of bile or its passage into the intestines is arrested, is a sufficient indication of the importance of this fluid. It acts as a stimulus to the intestinal canal generally, and produces on the chyme some peculiar change, which is essential to its conversion into chyle.

Biliary Concretions.

The concretions which are sometimes formed in the human gall-bladder have been particularly examined by Fourcroy, Thenard, and Chevreul. Fourcroy found that they consist chiefly of a peculiar fatty matter, resembling spermaceti, which he included under the name of *adipocire* (page 600); and the experiments of Thenard tended to confirm this view. According to Chevreul, however, biliary concretions in general are composed of the yellow colouring matter of the bile and cholsterine, the latter predominating, and being sometimes in a state of purity; and I have had frequent opportunities of satisfying myself of the accuracy of this observation. These substances may easily be separated from each other by boiling alcohol, which dissolves the cholesterine, and leaves the colouring matter; or by digestion in dilute potassa, in which the colouring matter is dissolved, while the cholesterine is insoluble.

Gall-stones sometimes contain a portion of inspissated bile; and in some rare instances the cholesterine is entirely wanting.

The concretions found in the gall-bladder of the ox consist almost entirely of the yellow biliary colouring matter, which, from the beauty and permanence of its tint, is much valued by painters. This substance is readily distinguished by its yellow or brown colour, by insolubility in water and alcohol, and by being readily dissolved by a solution of potassa. The solution has at first a yellowish-brown colour, which gradually acquires a green tint, and is precipitated in green flocks by hydrochloric acid. According to the observations of Tiedemann and Gmelin, the colouring matter is influenced by the presence of oxygen gas. The yellowish precipitate, occasioned by adding hydrochloric acid to bile, absorbs oxygen by exposure to the air, and its colour changes to green. The action of nitric acid is still more remarkable. By successive additions of this acid, the tint of the colouring matter may be converted into green, blue, violet, and red, in the course of a few seconds.

Erythrogen.—This substance was discovered in 1821 by M. Bizio of Venice in a peculiar fluid, quite different from bile, which was found in the gall-bladder of a person who had died of jaundice. It is of a green colour, transparent, tasteless, and of the odour of putrid fish. It is unctuous to the touch, may be scratched or cut with facility, and has a specific gravity of 1.57. It does not affect the colour of litmus or turmeric paper. At 110° it fuses, having the appearance of oil, and crystallizes when slowly cooled; and at 122° it rises in the form of vapour. It is insoluble in water and ether, but is dissolved readily by hot alcohol; and the solution, by partial evaporation and cooling, yields crystals in the form of rhomboidal parallelopipedons.

When erythrogen is put into nitric acid of the temperature of about 120 or 140° its green tint disappears, effervescence, owing to the escape of oxygen gas, ensues, and the solution acquires a deep purple colour. A similar phenomenon takes place, with disengagement of hydrogen gas, when erythrogen is digested in a solution of ammonia; and when volatilized in the open air, it yields a purple-coloured vapour. M. Bizio is of opinion that the erythrogen, under all these circumstances, unites with nitrogen, and that the product is identical with the colouring matter of the blood. The production of the red compound is characteristic of erythrogen, and suggested the name by which this substance is designated. (Εϱυθϱος, *ruber*). (Journal of Science, vol. xvi.)

Erythrogen has not been discovered either in bile or in any of the animal fluids.

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SECTION III.

CHYLE, MILK, AND EGGS.

Chyle.—THE fluid absorbed by the lacteal vessels from the small intestines during the process of digestion is known by the name of *chyle*. Its appearance varies in different animals; but as collected from the thoracic duct of a mammiferous animal three or four hours after a meal, it is a white opaque fluid like milk, having a sweetish and slightly saline taste. In a few minutes after removal from the duct it becomes solid, and in the course of twenty-four hours separates into a firm coagulum, and a limpid liquid, which may be called the serum of the chyle. The coagulum is an opaque white substance, of a slightly pink hue, insoluble in water, but soluble easily in the alkalies and alkaline carbonates. Vauquelin[*] regards it as fibrin in an imperfect state, or as intermediate between that principle and albumen; but Mr. Brande[†] considers it more closely allied to the caseous matter of milk than to fibrin.

The serum of chyle is rendered turbid by heat, and a few flakes of albumen are deposited; but when boiled after being mixed with acetic acid, a copious precipitation ensues. To this substance, which thus differs slightly from albumen, Dr. Prout has applied the name of *incipient albumen.* The same chemist has made a comparative analysis of the chyle of two dogs, one of which was fed on animal and the other on vegetable substances, and the result of his inquiry is as follows:—(Annals of Philos. vol. xiii. p. 25.)

	Vegetable Food.	Animal Food.
Water	93.6	89.2
Fibrin	0.6	0.8
Incipient albumen?	4.6	4.7
Albumen with a little red colouring matter	0.4	4.6
Sugar of milk?	a trace	—
Oily matters	a trace	a trace
Saline matters	0.8	0.7
	100.0	100.0

Milk.—This well-known fluid, secreted by the females of the class *mammalia* for the nourishment of their young, consists of three distinct parts, the cream, curd, and whey, into which by repose it spontaneously separates. The cream, which collects upon its surface, is an unctuous yellowish-white opaque fluid, of agreeable flavour. According to Berzelius 100 parts of cream, of specific gravity 1.0244, consist of butter 4.5, caseous matter 3.5, and whey 92. By agitation, as in the process of churning, the butter assumes the solid form, and is thus obtained in a separate state. During the operation there is an increase of temperature amounting to about three or four degrees, oxygen gas is absorbed, and an acid is generated; but the absorption of oxygen cannot be an essential part of the process, since butter may be obtained by churning, even when atmospheric air is entirely excluded.

After the cream has separated spontaneously, the milk soon becomes sour, and gradually separates into a solid coagulum called curd, and a limpid fluid which is whey. This coagulation is occasioned by free acetic acid, and it may be produced at pleasure either by adding a free acid, or by means of the fluid known by the name of *rennet*, which is made by infusing the inner coat of a calf's stomach in hot water. When an acid is employed, the curd is found to contain some of it in combination, and may, therefore, be regarded as an insoluble compound of an acid with the caseous matter of milk. The action of rennet requires further examination: it confessedly acts by means of the gastric fluid which it contains, and hence its coagulating power, consistently with the facts stated in the last section, is referable to the acidity of that juice.

The curd of skim milk, made by means of rennet, and separated from the whey by washing with water, is generally considered to be *caseous matter*, or the basis of cheese in a state of purity. In this state it is a white, insipid, inodorous substance, insoluble in water, but readily soluble in the alkalies, especially in ammonia. By alcohol it is converted, like albumen and fibrin, into an adipocirous substance of a fetid odour; and, like the same substance, it may be dissolved by a sufficient quantity of acetic acid.

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[*] An. de Ch. vol. xxxi.

[†] Philos. Trans. for 1812.

Braconnot maintains that caseum, in its coagulated state, is always combined with some foreign substance, generally an earthy salt or an acid, on which its insolubility depends; and that when pure, it is soluble both in hot and cold water, is not coagulated either by heat or air, and when concentrated becomes viscid like mucilage, being so highly adhesive that it may be usefully employed as a cement. Soluble caseum may be obtained from curd, spontaneously formed in milk as it becomes sour, in which state it is combined with acetic acid, by washing the curd, and digesting it with water, to which so much carbonate of potassa is added as is sufficient to unite with the acetic acid. Acetate of potassa is generated with disengagement of carbonic acid, and the caseum is dissolved. In order to separate it from the accompanying acetate, the solution, after separating the cream which collects on its surface by repose, is mixed with a little sulphuric acid, and the precipitated *sulphate* of caseum, carefully washed, is dissolved in water by means of the smallest possible quantity of carbonate of potassa. If alcohol is then freely employed, the caseum itself is thrown down; but if the solution is mixed with about its own volume of alcohol, a deposite of sulphate of potassa with some curd and cream takes place, and the filtered liquor contains caseum in a state of great purity.

Caseum, as thus prepared, still contains a little potassa; but Braconnot considers its solubility as not dependent on the presence of the alkali. When evaporated to dryness it forms a diaphanous mass which strongly resembles gum-arabic, may be long preserved without change, and still retains its solubility in water. It has an acid reaction, and combines readily with the alkalies, forming very soluble compounds. With other metallic oxides, as well as with their salts, it forms sparingly soluble compounds. Its affinity for acids is equally marked, and it is precipitated by all the mineral acids, except the phosphoric. Braconnot conceives that soluble caseum may be advantageously employed in a commercial point of view. Its adhesiveness fits it as a cement for glass, porcelain, wood, and paper. Its solution, flavoured with sugar and aromatics, may be serviceable to convalescents as an article of food. It may be taken in its dry state in long voyages, forming together with water, butter, and sugar, an excellent substitute for milk. (An. de Ch. et de Ph. xliii. 337.)

Caseum is commonly considered to have a close resemblance to animal albumen, and the analogy is supported by its being coagulated by acids. In other respects, if the remarks of Braconnot prove correct, it resembles gum rather than albumen. It differs from both, however, in the nature of the spontaneous changes to which it is subject; for when kept in a moist state, it undergoes a species of fermentation precisely analogous to that experienced by gluten under the same circumstances (page 568). The accuracy of the remarks made by Proust on this subject has been questioned by Braconnot (Brewster's Journal, viii. 369). The latter states that, in his experiments, the curd from spontaneously coagulated skim milk, covered with water, and kept at a temperature of about 75°, underwent complete putrefaction in the space of a month. The soluble parts were then filtered, and by evaporation yielded a product of a very fetid odour, acetate of ammonia, and acetic acid. The residue, after being reduced to the consistence of syrup, concreted on cooling into a granulated reddish mass like honey, but of a saline bitter taste, and was separated by the action of alcohol into two parts, one soluble and the other insoluble. The former is the caseate of ammonia of Proust, and the latter is his caseous oxide.

In order to obtain caseous oxide quite pure, it must be washed carefully with alcohol, treated with animal charcoal, and dissolved repeatedly in boiling water, from which it is separated by evaporation. In this state it is a beautiful white powder, inodorous, and of a slightly bitter taste. It is heavier than water, and soluble in 14 parts of that fluid at 72°. On allowing the solution to evaporate spontaneously, it crystallizes either in the form of elegant dendritic ramifications, or in rings composed of delicate acicular crystals of a silky lustre.

Caseous oxide is almost entirely insoluble even in boiling alcohol. Its aqueous solution yields a white flaky precipitate with infusion of gall-nuts, soluble in excess of the precipitant; and subacetate of lead likewise throws down a white precipitate. The crystals, if suddenly heated, volatilize without change; but if the heat is gradually raised, decomposition ensues, and a large quantity of carbonate and hydrosulphate of ammonia is generated. When strongly heated in open vessels it takes fire, and burns with flame without residue.

The composition of caseous oxide has not been determined, but from the facility with which its aqueous solution putrefies, Braconnot regards it as a highly azotized animal principle. It contains sulphur also. He believes it to be a product of the putrefaction of all animal substances, and proposes for it the name of *aposepedine*, from απο and σηπεδων, result of putrefaction, as more appropriate than caseous oxide.

Braconnot denies the existence of caseic acid. Proust's caseate of ammonia consists of various substances, such as free acetic acid, aposepedine, animal matter, resin, several salts, and a yellow pungent oil, which is the chief cause of the pungency of old cheese.

From 750 parts of curd completely putrefied were obtained 36 of dry matter insoluble in water. These consisted of 14.92 parts of margarate of lime, 2.57 of margaric acid, and 18.51 of oleic acid, retaining margaric acid and a brown animal matter.

According to the analysis of Gay-Lussac and Thenard, 100 parts of the caseous matter are composed of carbon 59.781, hydrogen 7.429, oxygen 11.409, and nitrogen 21.381. It yields by incineration a white ash amounting to 6.5 per cent. of its weight, the greater part of which is phosphate of lime, a circumstance which renders caseous matter an article of food peculiarly proper for young animals.

Milk carefully deprived of its cream has a specific gravity of about 1.033; and 1000 parts of it, according to Berzelius, are thus constituted:—water 928.75, caseous matter with a trace of butter 28; sugar of milk 35; muriate and phosphate of potassa 1.95; lactic acid, acetate of potassa, and a trace of lactate of iron 6, and earthy phosphates 0.3. Subtracting the caseous matter, the remaining substances constitute whey.

Eggs.—The composition of the recent egg and the changes which it undergoes during the process of incubation have been ably investigated by Dr. Prout (Phil. Trans. for 1822). New-laid eggs are rather heavier than water; but they become lighter after a time, in consequence of water evaporating through the pores of the shell, and air being substituted for it. An egg of ordinary size yields to boiling water about three-tenths of a grain of saline matter, consisting of the sulphates, carbonates, and phosphates of lime and magnesia, together with animal matter and a little free alkali.

Of an egg which weighs 1000 grains, the shell constitutes 106.9, the white 604.2, and the yelk 288.9 grains. The shell contains about two per cent. of animal matter, one per cent. of the phosphates of lime and magnesia, and the residue is carbonate of lime with a little carbonate of magnesia.

When the yelk of a hard-boiled egg is repeatedly digested in alcohol of specific gravity 0.807, until that fluid comes off colourless, there remains a white pulverulent residuum, possessed of many of the properties of albumen, but distinguished from that principle by containing a large quantity of phosphorus in some unknown state of combination. The alcoholic solution is of a deep yellow colour, and on cooling deposites crystals of a sebaceous matter, and a portion of yellow semi-fluid oil. On distilling off the alcohol, the oil is left in a separate state. When the yelk is dried and burned, the phosphorus is converted into phosphoric acid, which, melting into a glass upon the surface of the charcoal, protects it from complete combustion. In the white of the egg, which consists chiefly of albumen, sulphur is present.

The obvious use of the phosphorus contained in the yelk is to supply phosphoric acid for forming the bones of the chick; but Dr. Prout was unable to discover any source of the lime with which that acid unites to form the earthy part of bone. It cannot be discovered in the soft parts of the egg; and hitherto no vascular connexion has been traced between the chick and its shell.

SECTION IV.

LIQUIDS OF SEROUS AND MUCOUS SURFACES, &c.

THE surface of the cellular membrane is moistened with a peculiar limpid transparent fluid called *lymph*, which is in very small quantity during health, but collects abundantly in some dropsical affections. Mr. Brande collected it from the thoracic duct of an animal which had been kept without food for twenty-four hours. Its chief constituent is water, besides which it contains muriate of soda and albumen, the latter being in such minute quantity that it is coagulated only by the action of galvanism. Lymph does not affect the colour of test-paper; but when evaporated to dryness, the residue gives a green tint to the syrup of violets.

The fluid secreted by serous membranes in general, such as the pericardium, pleura, and peritoneum, is very similar to lymph. According to Dr. Bostock, 100 parts of the liquid of the pericardium consist of water 92 parts, albumen 5.5, mucus 2, and muriate of soda 0.5. The serous fluid exhaled within the ventricles of the brain in *hydrocephalus internus* is composed, in 1000 parts, of water 988.3, albumen 1.66, muriate of potassa and soda 7.09, lactate of soda and its animal matter 2.32, soda 0.28, and animal matter soluble only in water, with a trace of phosphates, 0.35. (Berzelius, in Medico-Chir. Trans. vol. iii. p. 252.)

The *liquor of the amnios*, or the fluid contained in the membrane which surrounds the *fœtus in utero*, differs in different animals. That of the human female was found by Vauquelin and Buniva to contain a small quantity of albumen, soda, muriate of soda, phosphate and carbonate of lime, and a matter like curd which gives it a milky appearance. That of the cow was said by the same chemists to contain a peculiar acid, which has since been recognized as belonging to the allantois (page 596). Dr. Prout found some sugar of milk in the amnios of a woman. (An. of Phil. v. 417.)

Humours of the Eye.—The aqueous and vitreous humours of the eye contain rather more than 80 per cent. of water. The other constituents are a small quantity of albumen, muriate and acetate of soda, pure soda, though scarcely sufficient to affect the colour of test-paper, and animal matter soluble only in water, but which is not gelatin. (Berzelius.) The crystalline lens, besides the usual salts, contains 36 per cent. of a peculiar animal matter, very analogous to albumen if not identical with it. In cold water it is soluble, but is coagulated by boiling. The coagulum, according to Berzelius, has all the properties of the colouring matter of the blood excepting its colour.

The *tears* are limpid and of a saline taste, dissolve freely in water, and, owing to the presence of free soda, communicate a green tint to the blue infusion of violets. Their chief salts are chloride of sodium and phosphate of soda. According to Fourcroy and Vauquelin the animal matter of the tears is mucus; but it is more probably either albumen, or some analogous principle. Its precise nature has not however been satisfactorily determined.

Mucus.—The term *mucus* has been employed in very different significations. Dr. Bostock applies it to a peculiar animal matter which is soluble both in hot and cold water, is not precipitated by corrosive sublimate or solution of tannin, is not capable of forming a jelly, and which yields a precipitate with subacetate of lead. The existence of this principle has not, however, been fully established; for the presence of muriatic and phosphoric acids, the latter of which is frequently contained in animal fluids, and the former scarcely ever absent, sufficiently accounts for the precipitates occasioned in them by the salts of lead or silver. But even supposing the opinion of Dr. Bostock to be correct, it would be advisable to give some new name to his principle, and apply the term *mucus* solely to the fluid secreted by mucous surfaces.

The properties of mucus vary somewhat according to the source from which it is derived; but its leading characters are in all cases the same, and are best exemplified in mucus from the nostrils. Nasal mucus, according to Berzelius, has the following properties. Immersed in water, it imbibes so much of that fluid as to become transparent, with the exception of a few particles which remain opaque. When dried on blotting-paper, it loses its transparency, but again acquires it when moistened. It is not coagulated or rendered horny by being boiled in water; but as soon as the ebullition has ceased, it collects unchanged at the bottom of the vessel. It is dissolved by dilute sulphuric acid. Nitric acid at first coagulates it; but by continued digestion, the mucus gradually softens and is finally dissolved, forming a clear yellow liquid. Acetic acid hardens mucus, and does not dissolve it even at a boiling temperature. Pure potassa at first renders it more viscid, but afterwards dissolves it. By tannic acid mucus is coagulated, both when softened by the absorption of water, and when dissolved either in an acid or an alkali.

Pus.—Purulent matter is the fluid secreted by an inflamed and ulcerated surface. Its properties vary according to the nature of the sore from which it is discharged. The purulent matter formed by an ill-conditioned ulcer is a thin, transparent, acrid, fetid ichor; whereas a healing sore in a sound constitution yields a yellowish-white coloured liquid, of the consistence of cream, which is described as bland, opaque, and inodorous. This is termed healthy pus, and is possessed of the following properties. Though it appears homogeneous to the naked eye, when examined with the microscope it is found to consist of minute globules floating in a transparent liquid. Its specific gravity is about 1.03. It is insoluble in water, and it is thickened, but not dissolved, by alcohol. When recent, it does not affect the colour of test-paper; but by exposure to the air it becomes acid. The dilute acids have little effect upon it; but strong sulphuric, nitric, and muriatic acids dissolve it, and the pus is thrown down by dilution with water. Ammonia reduces it to a transparent jelly, and gradually dissolves a considerable portion of it. With the fixed alkalies it forms a whitish ropy fluid, which is decomposed by water.

The composition of pus has not been ascertained with precision; but its characteristic ingredient is more closely allied to albumen than the other animal principles.

Several attempts have been made to discover a chemical test for distinguishing pus from mucus. When these fluids are in their natural state, the appearance of each is so characteristic that the distinction cannot be attended with any difficulty; but, on the contrary, when a mucous surface is inflamed, its secretion becomes opaque, and, as sometimes happens in some pulmonary diseases, acquires more or less of the aspect of pus. Mr. Charles Darwin, who examined this subject, pointed out three grounds of distinction between them. 1. When the solution of these liquids in sulphuric acid is diluted, the pus subsides to the bottom, and the mucus remains suspended in the water. 2. When pus and catarrhal mucus are diffused through water, the former sinks, and the latter floats. 3. Pus is precipitated from its solution in potassa by water, while the solution of mucus is not decomposed by similar treatment. Dr. Thomson, in his System of Chemistry, has given the following test on the authority of Grasmeyer. The substance to be examined, after being triturated with its own weight of water, is mixed with an equal quantity of a saturated solution of carbonate of potassa. If it contain pus, a transparent jelly forms in a few hours; but this does not happen if mucus only is present. Dr. Young, in his work on Consumptive Diseases, has given a very elegant character for distinguishing pus, founded on its optical properties. But the practical utility of tests of any kind is rendered very questionable by the fact that inflamed mucous membranes may secrete genuine pus without breach of surface, and that the natural passes into purulent secretion by insensible shades.

Sweat.—Watery vapour is continually passing off by the skin in the form of insensible perspiration; but when the external heat is considerable, or violent bodily exercise is taken, drops of fluid collect upon the surface, and constitute what is called sweat. This fluid consists chiefly of water; but it contains some muriate of soda and free acetic acid, in consequence of which it has a saline taste and an acid reaction.

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SECTION V.

URINE AND URINARY CONCRETIONS.

Urine.

The urine differs from most of the animal fluids which have been described by not serving any ulterior purpose in the animal economy. It is merely an excretion designed for ejecting from the system substances, which, by their accumulation within the body, would speedily prove fatal to health and life. The sole office of the kidneys, indeed, appears to consist in separating from the blood the superfluous matters that are not required or adapted for nutrition, or which have already formed part of the body, and been removed by absorption. The substances which in particular pass off by this organ are nitrogen, in the form of highly azotized products, and various saline and earthy compounds. This sufficiently accounts for the great diversity of different substances contained in urine.

The quantity of the urine is affected by various causes, especially by the nature and quantity of the liquids received into the stomach; but on an average, a healthy person voids between thirty and forty ounces daily. The quality of this fluid is likewise influenced by the same circumstances, being sometimes in a very dilute state, and at others highly concentrated. The urine voided in the morning by a person who has fed heartily, and taken no more fluids than is sufficient for satisfying thirst, may be regarded as affording the best specimen of natural healthy urine.

The urine in this state is a transparent limpid fluid of an amber colour, having a saline taste, and while warm emitting an odour which is slightly aromatic, and not at all disagreeable. The average sp. gr. of the urine of fifty healthy men, observed by the late Dr. Gregory in autumn at mid-day, is 1.02246. It gives a red tint to litmus paper, a circumstance which indicates the presence either of a free acid or of a supersalt. Though at first quite transparent, an insoluble matter is deposited on standing; so that urine, voided at night, is found to have a light cloud floating in it by the following morning. This substance consists in part of mucus from the urinary passages, and partly of superurate of ammonia, which is much more soluble in warm than in cold water.

The urine is very prone to spontaneous decomposition. When kept for two or three days it acquires a strong urinous smell; and as the putrefaction proceeds, the disagreeable odour increases, until at length it becomes exceedingly offensive. As soon as these changes commence, the urine ceases to have an acid reaction, and the earthy phosphates are deposited. In a short time, a free alkali makes its appearance, and a large quantity of carbonate of ammonia is gradually generated. Similar changes may be produced in recent urine by continued boiling. In both cases the phenomena are owing to the decomposition of urea, which is almost entirely resolved into carbonate of ammonia.

The composition of the urine has been studied by several chemists, but the most recent and elaborate analysis of this fluid is by Berzelius. According to the researches of this indefatigable chemist, 1000 parts of urine are composed of

Water	933.00
Urea	30.10
Uric acid	1.00
Free lactic acid, lactate of ammonia, and animal matter not separable from them	17.14
Mucus of the bladder	0.32
Sulphate of potassa	3.71
Sulphate of soda	3.16
Phosphate of soda	2.94
Phosphate of ammonia	1.65
Muriate of soda	4.45
Muriate of ammonia	1.50
Earthy matters, with a trace of fluate of lime	1.00
Siliceous earth	0.03

Besides the ingredients included in the preceding list, the urine contains several other substances in small quantity. From the property this fluid possesses of blackening silver vessels in which it is evaporated, owing to the formation of sulphuret of silver, Proust inferred the presence of unoxidized sulphur; and Dr. Prout, from the odour of phosphuretted hydrogen, which he thinks he has perceived in putrefying urine, suspects that phosphorus is likewise present. The urine also contains a peculiar yellow colouring matter which has not hitherto been obtained in a separate state. From the precipitate occasioned in urine by the infusion of gall-nuts, the presence of gelatin has been inferred; but this effect appears owing to the presence not of gelatin but of a small portion of albumen.

According to Scheele, the urine of infants sometimes contains benzoic acid, a compound which, when present, may be easily procured by evaporating the urine nearly to the consistence of syrup, and adding hydrochloric acid. The precipitate, consisting of uric and benzoic acids, is digested in alcohol, which dissolves the benzoic acid.

Notwithstanding the high authority of Berzelius, it is very doubtful if any free acid be present in healthy urine. Dr. Prout, with every appearance of reason, maintains that the acidity of recent urine is occasioned by super-salts, and not by uncombined acid. He is of opinion that the acid reaction is chiefly, if not wholly, to be ascribed to the superphosphate of lime and superurate of ammonia, salts which he finds may co-exist in a liquid without mutual decomposition. A very strong argument, which to me indeed appears conclusive, in favour of this view, is derived from the fact, that on adding hydrochloric acid to recent urine, minute crystals of uric acid are gradually deposited, as always happens when this acid subsides slowly from a state of solution; but, on the contrary, if no free acid is added, an amorphous sediment, which Dr. Prout regards as superurate of ammonia is obtained.

Such is the general view of the composition of human urine in its natural healthy state. But this fluid is subject to a great variety of morbid conditions, which arise either from the deficiency or excess of certain principles which it ought to contain, or from the presence of others wholly foreign to its composition. As the study of these affections affords an interesting example of the application of chemistry to pathology and the practice of medicine, I shall briefly mention some of the most important morbid states of this fluid, referring for more ample details to the excellent treatise of Dr. Prout.*

Of the substances which, though naturally wanting, are sometimes contained in the urine, the most remarkable is sugar, which is secreted by the kidneys in diabetes (page 592). Diabetic urine has a sweet taste, and yields a syrup by evaporation, is almost always of a pale straw colour, and in general has a greater specific gravity than ordinary urine. A specimen of diabetic urine, the sp. gr. of which was 1.03626, was found by Mr. Kane to contain in 1000 parts, 913 of water, 60 of sugar, 6.5 of urea, and 20 of salts (Dublin Journal of Science, i. 20). Owing to the large quantity of sugar and the dilute state of the urea, diabetic urine has little tendency to putrefy, and is susceptible of undergoing the vinous fermentation.

The acidifying process which is constantly going forward in the kidneys, as evinced by the formation of sulphuric, phosphoric, and uric acids, sometimes proceeds to a morbid extent, in consequence of which two acids, the oxalic and nitric, are generated, neither of which exists in healthy urine. The former, by uniting with lime, gives rise to one of the worst kinds of urinary concretions; and the latter, in the opinion of Dr. Prout, leads to the production of purpurate of ammonia, by reacting on uric acid.

In severe cases of jaundice, the bile passes from the blood into the kidneys, and communicates a yellow colour to the urine. The most delicate test of its presence is hydrochloric acid, which causes a green tint.

Though albumen is contained in very minute quantity in healthy urine, in some diseases it is present in large proportion. According to Dr. Blackall it is characteristic of certain kinds of dropsy, accompanied with an inflammatory diathesis, as in that which supervenes in scarlet fever; and Dr. Prout has described two cases of albuminous urine, in which, without any febrile symptoms, albumen existed in such quantity that spontaneous coagulation took place within the bladder. Dr. Bright, in his Medical Reports, has shown that dropsical effusions with albuminous urine are often associated with disease of the kidney, and his observations have been confirmed by the experience of Dr. Christison and the late Dr. Gregory (Edin. Med. and Surg. Journal for Oct. 1829, Oct. 1831, and Jan. 1832). In this affection the urine is scanty, and its sp. gravity, from deficient quantity of saline matter and urea, is lower than natural, being in the average of 50 cases 1.01318, and is rarely so high as 1.02: this is so constant, that scanty albuminous urine of a low sp. gravity was considered by Dr. Gregory as nearly a sure indication of renal disease. The albumen is readily detected by the coagulating effect of heat or by ferrocyanuret of potassium (page 589), the urine if not acid, which it frequently is, being always previously acidulated by acetic acid. In the blood of patients suffering under renal disease with albuminous urine, Dr. Bostock detected a crystalline substance resembling urea, and Dr. Christison, pursuing the inquiry, obtained urea with all its characteristic properties.

Urea is secreted less abundantly than usual during inflammatory affections of the liver, whether acute or chronic, in the renal disease just mentioned, and during the hysteric paroxysm, in which latter affection the saline ingredients of the urine are secreted in unusual quantity. Urea is said to be wanting in diabetic urine, an error caused by the presence of sugar diminishing the tendency of nitrate of urea to crystallize. Dr. Henry has shown that urea, when mixed with a considerable proportion of sugar, cannot be discovered by the usual test of nitric acid; and, consequently, though present in diabetic urine, it may easily be overlooked. He has succeeded in detecting it in such cases by distillation, urea being the only known animal principle which is converted into carbonate of ammonia at a boiling temperature.

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* Inquiry into the Nature and Treatment of Gravel, Calculus, &c.

Mr. Kane has succeeded in separating the nitrate of urea in crystals by employing as the test nitric acid diluted with an equal weight of water, and plunging the mass into a freezing mixture of salt and ice. He has thus been able to prove that diabetic patients void in the course of 24 hours as much urea as healthy persons.

The mode by which Dr. Prout estimates the proportion of this principle is by putting the urine into a watch-glass, and carefully adding to it nearly an equal quantity of nitric acid, in such a manner that the acid may collect at the bottom. If spontaneous crystallization ensue, an excess of urea is indicated; and the degree of excess may be inferred approximately by marking the time which elapses before the effect takes place. Undiluted healthy urine yields crystals only after an interval of half an hour; but the nitrate crystallizes within that interval when the urea is in excess.

An unusually abundant secretion of uric acid is a circumstance by no means uncommon. In some instances this acid makes its appearance in a free state: but happily it generally occurs in combination with an alkali, especially with soda or ammonia. As the urates are much more soluble in warm than in cold water, the urine in which they abound is quite clear at the moment of being voided, but deposites a copious sediment in cooling. The undue secretion of these salts, if temporary, occasions scarcely any inconvenience, and arises from such slight causes, that it frequently takes place without being noticed. This affection is generally produced by errors in diet, whether as to quantity or quality, and by all causes which interrupt the digestive progress in any of its stages, or render it imperfect. Dr. Prout specifies unfermented heavy bread, and hard boiled puddings or dumplings, as in particular disposing to the formation of the urates. These sediments have commonly a yellowish tint, which is communicated by the colouring matter of the urine; or when they are deposited in fevers, forming the lateritious sediment, they are red, in consequence of the colouring matter of the urine being then more abundant. In fevers of an irritable nature, as in hectic, the sediment has often a pink colour, and is considered by Prout to consist of urate of ammonia coloured by purpurate of ammonia; but Messrs. Brett and Bird have examined several pink sediments, in all of which the colouring ingredient was a substance soluble in alcohol and not purpuric acid. (Medical Gazette, August 23, 1834.)

So long as uric acid remains in combination with a base, it never yields a crystalline deposite; but when this acid is in excess and in a free state, its very sparing solubility causes it to separate in minute crystals, even within the bladder, giving rise to two of the most distressing complaints to which human nature is subject,—to gravel when the crystals are detached from one another, and when agglutinated by animal matter into concrete masses, to the disease called the *stone*. These diseases may arise either from uric acid being directly secreted by the kidneys, or, as Dr. Prout suspects, from the formation of some other acid, by which the urate of ammonia is decomposed. The tendency of urine to contain free acid occurs most frequently in dyspeptic persons of a gouty habit, and is familiarly known by the name of the uric or lithic acid diathesis. In these individuals the disposition to undue acidity of the urine is superadded to that state of the system which leads to an unusual supply of the urates.

A deficiency of acid in urine is not less injurious than its excess. As phosphate of lime in its neutral state is insoluble in water, this salt cannot be dissolved in urine except by being in the form of a superphosphate. Hence it happens that healthy urine yields a precipitate, when it is neutralized by an alkali; and if, by the indiscriminate employment of alkaline medicines, or from any other cause, the urine, while yet within the bladder, is rendered neutral, the earthy phosphates are necessarily deposited, and an opportunity afforded for the formation of a stone.

Urinary Concretions.

The first step towards a knowledge of urinary calculi was made in the year 1776 by Scheele, who showed that many of the concretions formed in the bladder consist of uric or lithic acid. The subject was afterwards successfully investigated by Wollaston and Pearson in this country, and by Fourcroy and Vauquelin in France; but the merit of having first ascertained the composition and chemical characters of most of the species of urinary calculi at present known, belongs to Dr. Wollaston. (Phil. Trans. for 1797.) The chemists who have since materially contributed to advance our knowledge of this department of science, are Henry, Brande, Prout, and the late Dr. Marcet, to whose "Essay on the Chemical History and Medical Treatment of Calculous Disorders," I may refer the reader who is desirous of studying this important subject.

The most common kinds of urinary concretions may be conveniently divided into six species: 1. The uric acid calculus; 2. The bone-earth calculus, principally consisting of phosphate of lime; 3. The ammoniaco-magnesian phosphate; 4. The fusible calculus, being a mixture of the two preceding species; 5. The mulberry calculus, composed of oxalate of lime; and, lastly, the cystic oxide calculus. (Marcet.)

1. The uric acid forms a hard inodorous concretion, commonly of an oval form, of a brownish or fawn colour, and smooth surface. These calculi consist of layers arranged concentrically around a central nucleus, the laminæ being distinguished from each other by a slight difference in colour, and sometimes by the interposition of some other substance.

This species is readily distinguished by the following characters. It is very sparingly soluble in water and muriatic acid. Digested in pure potassa it quickly disappears, and on adding an acid to the solution, the uric acid is precipitated. It is dissolved with effervescence by nitric acid, and the solution yields purpurate of ammonia when evaporated. Before the blowpipe it becomes black, emits a peculiar animal odour, and is gradually consumed, leaving a trace of white ash, which has an alkaline reaction.

As a variety of this species may be mentioned urate of ammonia, a rare kind of calculus first noticed by Fourcroy. Brande and Marcet expressed a doubt of its ever forming an independent concretion; but its existence, as such, has been established by Prout. The calculus of urate of ammonia has the same general chemical characters as that composed of uric acid, from which it is distinguished by its solubility in boiling water, when reduced to powder, and by its solution in potassa being attended with the disengagement of ammonia. It deflagrates remarkably before the blowpipe. (Medico-Chir. Trans. x. 389.)

2. The bone-earth calculus, first correctly analyzed by Wollaston, consists of phosphate of lime. The surface of these calculi is of a pale brown colour, and quite smooth as if it had been polished. When sawed through the middle, they are found to be laminated in a very regular manner, and the layers in general adhere so slightly that they may be separated with ease into concentric crusts. Dr. Yellowly, in several bone-earth concretions, has detected small quantities of carbonate of lime, which appears to have been overlooked by others.

This calculus, when reduced to powder, dissolves with facility in dilute nitric or muriatic acid, but is insoluble in potassa. Before the blowpipe it first assumes a black colour, from the decomposition of a little animal matter, and then becomes quite white, undergoing no further change unless the heat be very intense, when it is fused.

3. Phosphate of ammonia and magnesia was first described as a constituent of urinary calculi by Wollaston. It rarely exists quite alone, because the same state of the urine which leads to the formation of this species, favours the deposition of phosphate of lime; but it is frequently the pre-

vailing ingredient. It often appears in the form of minute sparkling crystals, diffused over the surface or between the interstices of other calculous laminæ.

Calculi, in which this salt prevails, are generally white, and less compact than the foregoing species. When reduced to powder they are dissolved by cold acetic acid, and still more easily by the stronger acids, the salt being thrown down unchanged by ammonia. Digested in pure potassa, it emits an ammoniacal odour, but it is not dissolved. Before the blowpipe, a smell of ammonia is given out, it diminishes in size, and melts into a white pearl with rather more facility than phosphate of lime.

4. The fusible calculus, the nature of which was first determined by Wollaston, is a mixture of the two preceding species. It is commonly of a white colour, and its fracture is usually ragged and uneven. It is more friable than any of the other kinds of calculus, separates easily into layers, and leaves a white dust on the fingers. These concretions are very common, and sometimes attain a large size.

The fusible calculus is characterized by the facility with which it melts into a pearly globule, which is sometimes quite transparent. When reduced to powder, and put into cold acetic acid, the phosphate of ammonia and magnesia is dissolved, and the phosphate of lime, almost the whole of which is left, dissolves readily in hydrochloric acid.

5. The mulberry calculus, so named from its resemblance to the fruit of the mulberry, was first proved to consist of oxalate of lime by Wollaston. This concretion is sufficiently characterized by its dark-coloured tuberculated surface, and by being very hard and compact; but it may also be distinguished chemically by the following properties. Heated before the blowpipe, the oxalic acid is decomposed, and pure lime remains, which gives a strong brown stain to moistened turmeric paper. It is insoluble in the alkalies; but by digestion in carbonate of potassa, it is decomposed, and the insoluble carbonate of lime is left. When reduced to powder and digested in hydrochloric or nitric acid, a perfect solution is effected. It is not dissolved by acetic acid, a circumstance which distinguishes it from the ammoniaco-magnesian phosphate; and it is distinguished from phosphate of lime by being insoluble in phosphoric acid.

6. The cystic oxide was described by its discoverer Wollaston in the Philosophical Transactions for 1810. This concretion is not laminated, but appears as one uniform mass, confusedly crystallized through its whole substance, having somewhat the appearance of the ammoniaco-magnesian phosphate, though more compact. Before the blowpipe it emits a peculiarly fetid smell, quite distinct from that of uric acid, and is consumed. It is characterized by the great variety of reagents in which it is soluble. It is dissolved abundantly by the hydrochloric, nitric, sulphuric, and oxalic acids; by potassa, soda, ammonia, and lime-water; and even by the neutral carbonates of soda and potassa. It is insoluble in water, alcohol, bicarbonate of ammonia, and in the tartaric, citric, and acetic acids.

From the similarity which this substance bears to certain oxides in uniting both with acids and alkalies, Dr. Wollaston termed it an oxide, and gave it the name of *cystic*, on the supposition of its being peculiar to the bladder. Dr. Marcet, however, has found it in the kidney.

Cystic oxide is a rare species of calculus. In this country seven specimens only have been found;—two by Dr. Wollaston, two by Dr. Henry, and three by Dr. Marcet: Professor Stromeyer has met with two instances of it in one family, and in one of the cases, the cystic oxide was also detected in the urine. M. Lassaigne has likewise found it in a stone taken from the bladder of a dog. From the analysis of this chemist, 100 parts of cystic oxide are composed of carbon 36.2, hydrogen 12.8, oxygen 17, and nitrogen 34.

Dr. Prout found the urine, during the formation of cystic oxide calculus, to have a density varying from 1.020 to 1.022, to be rather abundant, faintly acid, of a yellowish-green colour and peculiar odour, and to contain very little uric acid and urea. A greasy-looking film of cystic oxide collected on its surface, and a copious pale precipitate was thrown down by bicarbonate of ammonia, consisting of cystic oxide and the ammoniaco-magnesian phosphate. The cystic oxide was also precipitated by acetic acid. Dr. Venables has examined the urine in a similar state, and made similar remarks. (Edin. Med. and Surg. Journal, Oct. 1830.)

It is remarkable that cystic oxide is never accompanied with the matter of any other concretion; whereas the other species are frequently met with in the same stone. They are sometimes so intimately mixed that they can be separated from one another only by chemical analysis, forming what is called a *compound* calculus; but more frequently the concretion consists of two or more different species arranged in distinct alternate layers. This is termed the *alternating* calculus.

Besides the calculi just mentioned, a few other species have been noticed. Two were described by Dr. Marcet under the names of *xanthic oxide* and *fibrinous calculus*, both of which are exceedingly rare. Xanthic oxide is of a reddish or yellow colour, is soluble both in acids and alkalies, and its solution in nitric acid, when evaporated, assumes a bright lemon-yellow tint, a property to which it owes its name, and by which it is characterized. (ξανθος *yellow.*) The fibrinous calculus derives its name from fibrin, to which its properties are closely analogous. The third species consists chiefly of carbonate of lime, and is likewise of rare occurrence. It is probable that in some very uncommon cases, silica forms the principal ingredient of a stone; at least siliceous matter was found by Dr. Venables to be voided in one if not in two cases of gravel. (Journal of Science, N. S. vi. 234.) He has since met with it in other cases.

From the solubility of urinary concretions in chemical menstrua, hopes were once entertained that reagents might be introduced into the urine through the medium of the blood, or be at once injected into the bladder, so as to dissolve urinary calculi, and thus supersede the necessity of a painful and dangerous operation. It has been found, however, that, for this purpose, it would be necessary to employ acid or alkaline solutions of greater strength than may safely be introduced into the bladder; and consequently all attempts of the kind have been abandoned. The last suggestion of this nature was made by Prevost and Dumas, who proposed to disunite the elements of calculi by means of galvanism. This agent, however, though it may produce this effect out of the body, will scarcely, I conceive, be found admissible in practice.

SECTION VI.

SOLID PARTS OF ANIMALS.

Bones consist of earthy salts and animal matter intimately blended, the former of which are designed for giving solidity and hardness, and the latter for agglutinating the earthy particles. The animal substances are chiefly cartilage, gelatin, and a peculiar fatty matter called marrow. On reducing bones to powder, and digesting them in water, the fat rises and swims upon its surface, while the gelatin is dissolved. By digesting bones in dilute hydrochloric acid, the earthy salts are dissolved, and a flexible mass remains which retains the original figure of the bone, and consists of gelatin and cartilage: the former is by far the most abundant, since nearly the whole may be dissolved in boiling water, and yields a solution possessed of all the properties of gelatin. The residual cartilage appears identical with coagulated albumen. The animal matter of bones is formed before the earthy matter, and constitutes the nidus in which the latter is deposited.

When bones are heated in close vessels, a large quantity of carbonate of ammonia, some fetid empyreumatic oil, and the usual inflammable gases pass over into the recipient; while a mixture of charcoal and earthy matter, called animal charcoal, remains in the retort. If, on the contrary, they are heated to redness in an open fire, the charcoal is consumed, and a pure white friable earth is the sole residue.

According to the analysis of Berzelius, 100 parts of dry human bones consist of animal matters 33.3, phosphate of lime 51.04, carbonate of lime 11.3, fluate of lime 2, phosphate of magnesia 1.16, and soda, muriate of soda, and water 1.2. Mr. Hatchett found, also, a small quantity of sulphate of lime; and Fourcroy and Vauquelin discovered traces of alumina, silica, and the oxides of iron and manganese.

Teeth are composed of the same materials as bone; but the enamel dissolves completely in dilute nitric acid, and, therefore, is free from cartilage. From the analysis of Mr. Pepys, the enamel contains 78 per cent. of phosphate and 6 of carbonate of lime, the residue being probably gelatin. The composition of ivory is similar to that of the bony matter of teeth in general.

The shells of eggs and the covering of crustaceous animals, such as lobsters, crabs, and the starfish, consist of carbonate and a little phosphate of lime and animal matter. The shells of oysters, muscles, and other molluscous animals consist almost entirely of carbonate of lime and animal matter, and the composition of pearl and mother of pearl is similar.

Horn differs from bone in containing only a trace of earth. It consists chiefly of gelatin and a cartilaginous substance like coagulated albumen. The composition of the nails and hoofs of animals is similar to that of horn; and the cuticle belongs to the same class of substances.

Tendons appear to be composed almost entirely of gelatin; for they are soluble in boiling water, and the solution yields an abundant jelly on cooling. The composition of the true skin is nearly the same as that of tendons. Membranes and ligaments are composed chiefly of gelatin, but they also contain some substance which is insoluble in water, and is similar to coagulated albumen.

According to the analysis of Vauquelin, the principal ingredient of hair is a peculiar animal substance, insoluble in water at 212° F. but which may be dissolved in that liquid by means of Papin's digester, and is soluble in a solution of potassa. Besides this substance hair contains oil, sulphur, silica, iron, manganese, and carbonate and phosphate of lime. The colour of the hair depends on that of its oil; and the effect of metallic solutions, such as nitrate of oxide of silver, in staining the hair, is owing to the presence of sulphur.

The composition of wool and feathers appears analogous to that of hair. The quill part of the feather was found by Mr. Hatchett to consist of coagulated albumen.

Silk is covered with a peculiar varnish which is soluble in boiling water and in alkaline solutions, and amounts to about 23 per cent. of the raw material. By digestion in alcohol it is also deprived of a portion of wax. The remaining fibrous structure has been examined in a very imperfect manner. By the action of nitric acid it is converted into carbazotic acid.

The flesh of animals, or *muscle*, consists essentially of fibrin; but independently of this principle, it contains several other ingredients, such as albumen, gelatin, a peculiar extractive matter called *osmazome*, fat, and salts, substances which are chiefly derived from the blood, vessels, and cellular membrane, dispersed through the muscles. On macerating flesh, cut into small fragments, in successive portions of cold water, the albumen, osmazome, and salts are dissolved; and on boiling the solution, the albumen is coagulated. From the remaining liquid, the osmazome may be procured in a separate state by evaporating to the consistence of an extract, and treating it with cold alcohol. By the action of boiling water, the gelatin of the muscle is dissolved, the fat melts and rises to the surface of the water, and pure fibrin remains.

The characteristic odour and taste of soup are owing to the osmazome. This substance is of a yellowish-brown colour, and is distinguished from the other animal principles by solubility in water and alcohol, whether cold or at a boiling temperature, and by not forming a jelly when its solution is concentrated by evaporation. Like gelatin and albumen it yields a precipitate with infusion of gall-nuts.

The substance of the brain, nerves, and spinal marrow differs from that of all other animal textures. The most elaborate analysis of cerebral matter is by Vauquelin, who found that 100 parts of it consist of water 80, albumen 7, white fatty matter 4.53, red fatty matter 0.7, osmazome 1.12, phosphorus 1.5, and acids, salts, and sulphur 5.15. (Annals of Phil. i.)

M. Couerbe has discovered in the brain a large quantity of cholesterine. He also states that the brain of persons of sound intellect usually contains from 2 to 2½ per cent. of phosphorus: in the brain of idiots the phosphorus is about 1 or 1½ per cent., and in maniacs it amounts to 3, 4, and 4½ per cent.

The presence of albumen accounts for the partial solubility of the brain in cold water, and for the solution being coagulated by heat, acids, alcohol, and by the metallic salts which coagulate other albuminous fluids. By acting upon cerebral matter with boiling alcohol, the fatty principles and osmazome are dissolved, and the solution in cooling deposites the white fatty matter in the form of crystalline plates. On expelling the alcohol by evaporation, and treating the residue with cold alcohol, the osmazome is taken up, and a fixed oil remains of a reddish-brown colour, and an odour like that of the brain itself, though much stronger. These two species of fat differ little from each other, and both yield phosphoric acid when deflagrated with nitre.

SECTION VII.

PUTREFACTION.

When dead animal matter is exposed to air, moisture, and a moderate temperature, it speedily runs into putrefaction, during which every trace of its original texture disappears, and products of a very offensive nature are generated. The most favourable temperature is from 60° to 80° or 90° F. Below 50° the process takes place tardily, and at 32° it is wholly arrested;—a fact, which is clearly evinced by the circumstance that the bodies of animals, which have been buried in snow or ice, are found unchanged after a long series of years. The necessity of a certain degree of moisture is shown by the facility with which the most perishable substances may be preserved when quite dry. The preservation of smoked meat is chiefly owing to this cause; and, for a like reason, animals buried in the dry sand of Arabia and Egypt have remained for years without change.

It is probable that when moisture and warmth concur, putrefaction in animal matter which has not been heated to 212° will take place independently of atmospheric influence. But when animal matter has been boiled, and is then, without subsequent exposure, completely protected from air, it may be preserved for years, even though moist and in a temperature favourable to putrefaction. The practice of preserving every kind of food, both animal and vegetable, now a subject of extensive commercial enterprise, affords ample demonstration of this statement. The mode generally adopted is the following. Into a tin vessel is placed any kind of food, such as joints of meat, fish, game, and vegetables, dressed for the table; and into the interstices is poured a rich gravy, care being taken to have the vessel completely full. A tin cover, with a small aperture, is then carefully fixed by solder; and while the whole vessel is perfectly full, and at the temperature of 212°, the remaining aperture is closed. As the ingredients within cool and contract, a vacuum is formed if the operation has been skilfully conducted, and the sides of the vessel are in consequence slightly pressed in by the weight of the atmosphere. In this state the vessel may be sent to tropical climates without fear of putrefaction; and the most delicate food of one country be thus eaten in its original perfection, in a distant region, many months or even years after its preparation.

For reasons formerly mentioned, animal matters commonly undergo putrefaction more rapidly than those which are derived from the vegetable kingdom (page 494); but they are not all equally disposed to putrefy. The acid and fatty principles are less liable to this change than urea, fibrin, and other analogous substances. The chief products to which their dissolution gives rise are water, ammonia, carbonic acid, and sulphuretted, phosphuretted, and carburetted hydrogen gases.

PART IV.

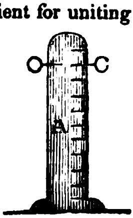
ANALYTICAL CHEMISTRY.

The object of this Fourth Part of the volume is to serve as a guide to those who purpose merely to skim the surface of analytical chemistry. To render it a complete manual was never intended: to do so would be foreign to the plan of these Elements, and would encroach on space which is devoted to another purpose. This part is, therefore, left without addition; and this is done the more willingly, because I hope at some future period to embody the results of my own experience in analytical chemistry in a separate volume. To those who are much occupied in the laboratory I would recommend the following works:—The Analytical Chemistry of Rose, either in the original German or the translation by Griffith, for processes of analysis; —Faraday's work on Chemical Manipulation for the delicate operations of research;—and Reid's Elements of Practical Chemistry for experiments of demonstration. The few following directions are thrown into three sections, which treat of the analysis of mixed gases, of minerals, and of mineral waters.

SECTION I.

ANALYSIS OF MIXED GASES.

Analysis of Air or of Gaseous Mixtures containing Oxygen.—Of the various processes by which oxygen gas may be withdrawn from gaseous mixtures, and its quantity determined, none are so convenient and precise as the method by means of hydrogen gas. In performing this analysis, a portion of atmospheric air is carefully measured in a graduated tube, and mixed with a quantity of hydrogen gas which is rather more than sufficient for uniting with all the oxygen present. The mixture is then introduced into a strong glass tube, A, called Volta's eudiometer, shown in the annexed wood-cut, and an electric spark is passed through it by means of the conducting wires B, B, fixed into the tube. The aperture is closed by the thumb at the moment of detonation, in order to prevent any of the mixture from escaping. The total diminution in volume, divided by three, indicates the quantity of oxygen originally contained in the mixture. This operation may be performed in a trough either of water or mercury.

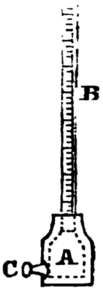


Instead of electricity, spongy platinum may be employed for causing the union of oxygen and hydrogen gases; and while its indications are very precise, it has the advantage of producing the effect gradually and without detonation. The most convenient mode of employing it with this intention is the following. A mixture of spongy platinum and pipe-clay, in the proportion of about three parts of the former to one of the latter, is made into a paste with water, and then rolled between the fingers into a globular form.

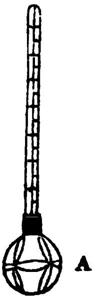
In order to preserve the spongy texture of the platinum, a little hydrochlorate of ammonia is mixed with the paste; and when the ball has become dry, it is cautiously ignited at the flame of a spirit-lamp. The sal ammoniac, escaping from all parts of the mass, gives it a degree of porosity which is peculiarly favourable to its action. The ball, thus prepared, should be protected from dust, and be heated to redness just before being used. To insure accuracy, the hydrogen employed should be kept over mercury for a few hours in contact with a platinum ball and a piece of caustic potassa. The first deprives it of traces of oxygen which it commonly contains, and the second of moisture and hydrosulphuric acid. The analysis must be performed in a mercurial trough. The time required for completely removing the oxygen depends on the diameter of the tube. If the mixture is contained in a very narrow tube, the diminution does not arrive at its full extent in less than twenty minutes or half an hour; while in a vessel of an inch in diameter, the effect is complete in the course of five minutes.

Mode of determining the Quantity of Nitrogen in Gaseous Mixtures.—As atmospheric air, which has been deprived of moisture and carbonic acid, consists of oxygen and nitrogen only, the proportion of the latter is of course known as soon as that of the former is determined. The only method, indeed, by which chemists are enabled to estimate the quantity of this gas, is by withdrawing the other gaseous substances with which it is mixed.

Mode of determining the Quantity of Carbonic Acid in Gaseous Mixtures.—When carbonic acid is the only acid gas which is present, as in analyzing atmospheric air, in the ultimate analysis of organic compounds, and in most other analogous researches, the process for determining its quantity is exceedingly simple; for it consists merely in absorbing that gas by lime-water or a solution of caustic potassa. This is easily done in the course of a few minutes in an ordinary graduated tube; or it may be effected almost instantaneously by agitating the gaseous mixture with the alkaline solution in Hopes's eudiometer. This apparatus, as represented in the figure, is formed of two parts:—of the bottle A, capable of containing about twenty drachms of fluid, and furnished with a well ground stopper C; and of the tube B, of the capacity of one cubic inch, divided into 100 equal parts, and accurately fitted by grinding to the neck of the bottle. The tube, full of gas, is fixed into the bottle previously filled with lime-water, and its contents are briskly agitated. The stopper C is then withdrawn under water, when a portion of liquid rushes into the tube, supplying the place of the gas which has disappeared; and the process is afterwards repeated, as long as any absorption ensues.



The eudiometer of Dr. Hope was originally designed for analyzing air or other similar mixtures, the bottle being filled with a solution of hydrosulphuret of potassa or lime, or some liquid capable of absorbing oxygen. To the employment of this apparatus it has been objected, that the absorption is rendered slow by the partial vacuum which is continually taking place within it, an inconvenience particularly felt towards the close of the process, in consequence of the eudiometric liquor being diluted by the admission of water. To remedy this defect, Dr. Henry has substituted a bottle of elastic gum for that of glass, as in the annexed wood-cut, by which contrivance no vacuum can occur. From the improved method of analyzing air, however, this instrument is now rarely employed in eudiometry; but it may be used with advantage for absorbing carbonic acid or similar gases, and is particularly useful for the purpose of demonstration.



Mode of analyzing Mixtures of Hydrogen and other Inflammable Gases.— When hydrogen is mixed with nitrogen, oxygen, or atmospheric air, its quantity is easily ascertained by causing it to combine with oxygen either by means of platinum or the electric spark. If, instead of hydrogen, any other combustible substance, such as carbonic oxide, light carburetted hydrogen, or olefiant gas, be mixed with nitrogen, the analysis is easily effected by adding a sufficient quantity of oxygen, and detonating the mixture by electricity. The diminution in volume indicates the quantity of hydrogen contained in the gas, and from the carbonic acid, which may then be removed by an alkali, the quantity of carbon is inferred.

An elegant mode of converting carbonic oxide into carbonic acid gas, suggested by Dr. Henry, is to mix it with rather more than its own volume of nitrous oxide gas, and fire the mixture by the electric spark. The two gases mutually decompose each other, and give rise to nitrogen and carbonic acid gases. For each measure of carbonic oxide one of carbonic acid is produced, one measure of nitrous oxide is decomposed, and one of nitrogen evolved. By employing a slight excess of pure carbonic oxide, the composition of nitrous oxide may be ascertained. The mixed gases occupy the same space after deflagration as before it; and the carbonic acid gas occupies the same space as the nitrous oxide which had been present. (Annals of Philosophy, xxiv. 301.)

When olefiant gas is mixed with other inflammable gases, its quantity is easily determined by an elegant and simple process proposed by Dr. Henry (page 249). It consists in mixing 100 measures, or any convenient quantity of the gaseous mixture, with an equal volume of chlorine in a vessel covered with a piece of cloth or paper, so as to protect it from light; and after an interval of about ten minutes, the excess of chlorine is removed by a solution of lime or potassa. The loss experienced by the gas to be analyzed, indicates the exact quantity of olefiant gas which it had contained.

This method is not correct when the vapours of the dense hydrocarburets are present. Thus when oil gas is mixed with chlorine, the diminution in volume arises from the removal of the combustible vapours as well as of olefiant gas; for the former are equally disposed as the latter to unite with chlorine.

In mixtures of hydrogen, carburetted hydrogen, and carbonic oxide, the analytic process is exceedingly difficult and complicated, and requires all the resources of the most refined chemical knowledge, and all the address of an experienced analyst. The most recent information on this subject will be found in Dr. Henry's Essay in the Philosophical Transactions for 1824.

SECTION II.

ANALYSIS OF MINERALS.

As the very extensive nature of this department of analytical chemistry renders a selection necessary, I shall confine my remarks solely to the analysis of those earthy minerals with which the beginner usually commences his labours. The most common constituents of these compounds are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and carbonic and sulphuric acids; and I shall, therefore, endeavour to give short directions for determining the quantity of each of these substances.

In attempting to separate two or more fixed principles from each other, the first object of the analytical chemist is to bring them into a state of solution. If they are soluble in water, this fluid is preferred to every other menstruum; but if not, an acid or any convenient solvent may be employed.

In many instances, however, the substance to be analyzed resists the action even of the acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate: it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

Analysis of Marble or Carbonate of Lime.—This analysis is easily made by exposing a known quantity of marble for about half an hour to a full white heat, by which means the carbonic acid gas is entirely expelled, so that by the loss in weight, the quantity of each ingredient, supposing the marble to have been pure, is at once determined. In order to ascertain that the whole loss is owing to the escape of carbonic acid, the quantity of this gas may be determined by a comparative analysis. Into a small flask containing hydrochloric acid diluted with two or three parts of water, a known quantity of marble is gradually added, the flask being inclined to one side in order to prevent the fluid from being flung out of the vessel during the effervescence. The diminution in weight experienced by the flask and its contents, indicates the quantity of carbonic acid which has been expelled.

Should the carbonate suffer a greater loss in the fire than when decomposed by an acid, it will most probably be found to contain water. This may be ascertained by heating a piece of it to redness in a glass tube, the sides of which will be bedewed with moisture, if water is present. Its quantity may be determined by causing the watery vapour to pass through a weighed tube filled with fragments of the chloride of calcium, by which the moisture is absorbed.

Separation of Lime and Magnesia.—The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute hydrochloric acid. A very frequent source of impurity is carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *magnesian limestone.* The analysis of this substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the following manner. The solution of the mineral in muriatic acid is evaporated to perfect dryness in a flat dish or *capsule* of porcelain, and after redissolving the residuum in a moderate quantity of distilled water, a solution of oxalate of ammonia is added as long as a precipitate ensues. The oxalate of lime is then allowed to subside, collected on a filter, converted into quicklime by a white heat, and weighed; or the oxalate may be decomposed by a red heat, and after moistening the resulting carbonate with a strong solution of carbonate of ammonia, in order to supply any particles of quicklime with carbonic acid, it should be dried, heated to low redness, and regarded as pure carbonate of lime. To the filtered liquid, containing the magnesia, a mixture of pure ammonia and phosphate of soda is added, when the magnesia in the form of the ammoniaco-phosphate is precipitated. Of this precipitate, heated to redness, 100 parts, according to Stromeyer, correspond to 37 of pure magnesia.

The precipitation of magnesia by means of phosphoric acid and ammonia, though extremely accurate when properly performed, requires several precautions. The liquid should be cold, and either neutral or alkaline. The precipitate is dissolved with great ease by most of the acids; and Stromeyer has remarked that some of it is held in solution by carbonic acid whether free or in union with an alkali. The absence of carbonic acid should, therefore, always be insured, prior to the precipitation, by heating the solution to 212°, acidulating at the same time by hydrochloric acid, should an alkaline carbonate be present. Berzelius has also observed, that in washing the ammoniaco-magnesian phosphate on a filter, a portion of the salt is dissolved as soon as the saline matter of the solution is nearly all removed; that is to say, it is dissolved by pure water. Hence the edulcoration should be completed by water, which is rendered slightly saline by hydrochlorate of ammonia.

Earthy Sulphates.—The most abundant of the earthy sulphates is that of lime, the analysis of which is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of carbonate of soda, double decomposition ensues; and the carbonate of lime, after being collected on a filter and washed with hot water, is either heated to low redness to expel the water, and weighed, or at once reduced to quicklime by a white heat. Of the dry carbonate, 50 parts correspond to 28 of lime. The alkaline solution is acidulated with hydrochloric acid, and the sulphuric acid thrown down by chloride of barium. From the sulphate of baryta, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphate of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted. The sulphate, in fine powder, is mixed with three times its weight of carbonate of soda, and the mixture is heated to redness in a platinum crucible for the space of an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

Mode of analyzing Compounds of Silica, Alumina, and Iron.—Minerals, thus constituted, are decomposed by an alkaline carbonate at a red heat, in the same manner as sulphate of baryta. The mixture is afterwards digested in dilute hydrochloric acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that on digesting the dry mass in water acidulated with hydrochloric acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefully edulcorated, heated to redness, and weighed.

To the clear liquid, containing peroxide of iron and alumina, a solution of pure potassa is added in moderate excess; so as not only to throw down those oxides, but to dissolve the alumina. The peroxide of iron is then collected on a filter, edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried on a sand-bath. Of this hydrated peroxide, 49 parts contain 40 of anhydrous peroxide of iron. But the most accurate mode of determining its quantity is by expelling the water by a red heat. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with hydrochlorate of ammonia, when chloride of potassium is formed, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

Separation of Iron and Manganese.—A compound of these metals or their oxides may be dissolved in hydrochloric acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage. To the cold solution considerably diluted with water, and acidulated with hydrochloric acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquid is then boiled with an excess of carbonate of soda; and the precipitated carbonate of manganese is collected, heated to full redness in an open crucible, by which it is converted into the red oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime as well as from manganese.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in the state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of peroxide of iron be washed with cold water. Of this succinate, well dried at a temperature of 212°, 90 parts correspond to 40 of the peroxide. From the filtered liquid the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for succinate of ammonia in the preceding process.

It may be stated as a general rule, that whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

Separation of Manganese from Lime and Magnesia.—If the quantity of the former be proportionally small, it is precipitated as a sulphuret by hydrosulphate of ammonia or sulphuret of potassium. The sulphuret is then dissolved in hydrochloric acid, and the manganese thrown down as usual by means of an alkali. But if the manganese be the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric acid, when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up, it may easily be thrown down by hydrosulphate of ammonia.

Stromeyer has recommended a very elegant and still better process for removing small quantities of manganese from lime and magnesia. The solution is acidulated with nitric or hydrochloric acid, bicarbonate of soda is gradually added in very slight excess, stirring after each addition, that the liquid may be charged with carbonic acid, and a solution of chlorine, or a current of the gas, is introduced. The protoxide of manganese is converted by the chlorine into the insoluble hydrated peroxide, while any traces of lime or magnesia, which might otherwise fall, are retained in solution by means of carbonic acid. A solution of chloride of soda or lime is in fact our most delicate test for small quantities of manganese.

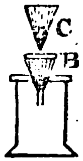
Mode of analyzing an Earthy Mineral containing Silica, Iron, Alumina, Manganese, Lime, and Magnesia.—The mineral, reduced to fine powder, is ignited with three or four times its weight of carbonate of potassa or soda, the mass is taken up in dilute hydrochloric acid, and the silica separated in the way already described. To the solution, thus freed from silica and duly acidulated, carbonate of soda, or still better the bicarbonate, is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances which may be separated from each other by means of pure potassa (page 641). The manganese, lime, and magnesia may then be determined by the processes above described.

Analysis of Minerals containing a Fixed Alkali.—When the object is to determine the quantity of fixed alkali, such as potassa or soda, it is of course necessary to abstain from the employment of these reagents in the analysis itself; and the beginner will do well to devote his attention to the alkaline ingredients only. On this supposition, he will proceed in the following manner. The mineral is reduced to a very fine powder, mixed intimately with six times its weight of artificial carbonate of baryta, and exposed for an hour to a white heat. The ignited mass is dissolved in dilute hydrochloric acid, and the solution evaporated to perfect dryness. The soluble parts are taken up in hot water; an excess of carbonate of ammonia is added; and the insoluble matters, consisting of silica, carbonate of baryta, and all the constituents of the mineral, excepting the fixed alkali, are collected on a filter. The clear solution is evaporated to dryness in a porcelain capsule, and the dry mass is heated to redness in a crucible of platinum, in order to expel the salts of ammonia. The residue is chloride of potassium or sodium.

In this analysis, it generally happens that traces of manganese, and sometimes of iron, escape precipitation in the first part of the process; and, in that case, they should be thrown down by hydrosulphate of ammonia. If neither lime nor magnesia is present, the alumina, iron, and manganese may be separated by pure ammonia, and the baryta subsequently removed by the carbonate of that alkali. By this method the carbonate of baryta is recovered in a pure state, and may be reserved for another analysis. The baryta may also be thrown down as a sulphate by sulphuric acid, in which case the soda or potassa is procured in combination with that acid; but this mode is objectionable, because the sulphate of baryta is very apt to retain small quantities of sulphate of potassa.

The analysis is attended with considerable inconvenience when magnesia happens to be present; because this earth is not completely precipitated either by ammonia or its carbonate, and, therefore, some of it remains with the fixed alkali. The best mode with which I am acquainted, is to precipitate the magnesia by phosphate of ammonia; subsequently separating from the filtered solution the excess of phosphoric acid by acetate of lead, and that of lead by hydrosulphuric acid. The acetate of the alkali is then brought to dryness, ignited, and by the addition of sulphate of ammonia converted into a sulphate.

In the preceding account, several operations have been alluded to, which, from their importance, deserve more particular mention. The process of filtering, for example, is one on which the success of analysis materially depends. Filtration is effected by means of a glass funnel B, into which a filter C, of nearly the same size and form, made of white bibulous paper, is inserted. For researches of delicacy, the filter, before being used, is macerated for a day or two in water acidulated with nitric acid, in order to dissolve lime and other substances contained in common paper, and it is afterwards washed with hot water till every trace of acid is removed. It is next dried at 212°, or any fixed temperature insufficient to decompose it, and then carefully weighed, the weight being marked upon it with a pencil. As dry paper absorbs hygrometric moisture rapidly from the atmosphere, the filter, while being weighed, should be inclosed in a light box made for the purpose. When a precipitate is collected on a filter, it is washed with pure water until every trace of the original liquid is removed. It is subsequently dried and weighed as before, and the weight of the paper subtracted from the combined weight of the filter and precipitate. The trouble of weighing the filter may sometimes be dispensed with. Some substances, such as silica, alumina, and lime, which are not decomposed when heated with combustible matter, may be put into a crucible while yet contained in the filter, the paper being set on fire before it is placed in the furnace. In these instances, the ash from the paper, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.



The tests commonly employed in ascertaining the acidity or alkalinity of liquids are litmus and turmeric paper. The former is made by digesting litmus, reduced to a fine powder, in a small quantity of water, and painting with it white paper which is free from alum. Turmeric paper is made in a similar manner; but the most convenient test of alkalinity is litmus paper reddened by a dilute acid.

SECTION III.

ANALYSIS OF MINERAL WATERS.

Rain water collected in clean vessels in the country, or freshly fallen snow when melted, affords the purest kind of water which can be procured without having recourse to distillation. The water obtained from these sources, however, is not absolutely pure, but contains a portion of carbonic acid and air, absorbed from the atmosphere. It is remarkable that this air is very rich in oxygen. That procured from snow water by boiling was found by Gay-Lussac and Humboldt to contain 34.8, and that from rain water 32 per cent. of oxygen gas. From the powerfully solvent properties of water, this fluid no sooner reaches the ground and percolates through the soil, than it dissolves some of the substances which it meets with in its passage. Under common circumstances it takes up so small a quantity of foreign matter, that its sensible properties are not materially affected; and in this state it gives rise to *spring*, *well*, and *river* water. Sometimes, on the contrary, it becomes so strongly impregnated with saline and other substances, that it acquires a peculiar flavour, and is thus rendered unfit for domestic uses. It is then known by the name of *mineral water*.

The composition of spring water is dependent on the nature of the soil through which it flows. If it has filtered through primitive strata, such as quartz rock, granite, and the like, it is in general very pure; but if it meets with limestone or gypsum in its passage, a portion of these salts is dissolved, and communicates the property called *hardness*. Hard water is characterized by decomposing soap, the lime of the former yielding an insoluble compound with the margaric and oleic acid of the latter. If this defect is owing to the presence of carbonate of lime, it is easily remedied by boiling, when free carbonic acid is expelled, and the insoluble carbonate of lime subsides. If sulphate of lime is present, the addition of a little carbonate of soda, by precipitating the lime, converts the hard into soft water. Besides these ingredients, the chlorides of calcium and sodium are frequently contained in spring water.

Spring water, in consequence of its saline impregnation, is frequently unfit for chemical purposes, and on these occasions distilled water is employed. Distillation may be performed on a small scale by means of a retort, in the body of which water is made to boil, while the condensed vapour is received in a glass flask, called a *recipient*, which is adapted to its beak or open extremity. This process is more conveniently conducted, however, by means of a still.

The different kinds of mineral water may be conveniently arranged for the purpose of description in the six divisions of *acidulous*, *alkaline*, *chalybeate*, *sulphuretted*, *saline*, and *siliceous* springs.

1. *Acidulous springs*, of which those of Seltzer, Spa, Pyrmont, and Carlsbad are the most celebrated, commonly owe their acidity to the presence of free carbonic acid, in consequence of the escape of which they sparkle when poured from one vessel into another. Such carbonated waters communicate a red tint to litmus paper before, but not after being boiled, and the redness disappears on exposure to the air. Mixed with a sufficient quantity of lime-water, they become turbid from the deposition of carbonate of lime. They

frequently contain the carbonates of lime, magnesia, and protoxide of iron, in consequence of the facility with which these salts are dissolved by water charged with carbonic acid.

The best mode of determining the quantity of carbonic acid is by heating a portion of the water in a flask, as in the annexed figure, and receiving the carbonic acid, by means of a bent tube, in a graduated jar filled with mercury.

2. *Alkaline waters* are such as contain a free or carbonated alkali, and, consequently, either in their natural state or when concentrated by evaporation, possess an alkaline reaction.

These springs are rare. The best instance I have met with is in water collected at the Furnas, St. Michael's, Azores, and sent to the Royal Society of Edinburgh by Lord Napier. These springs contain carbonate of soda and carbonic acid, and are almost entirely free from earthy substances. Of five different kinds of these waters which I examined, the greater part also contained protoxide of iron, hydrosulphuric acid, and chloride of sodium.

3. *Chalybeate waters* are characterized by a strong styptic, inky taste, and by striking a black colour with the infusion of gall-nuts. The iron is sometimes combined with hydrochloric or sulphuric acid; but most frequently it is in the form of protocarbonate, held in solution by free carbonic acid. On exposure to the air, the protoxide is oxidized, and the hydrated peroxide subsides, causing the ochreous deposite so commonly observed in the vicinity of chalybeate springs.

To ascertain the quantity of iron contained in a mineral water, a known weight of it is concentrated by evaporation, and the iron is brought to the state of peroxide by means of nitric acid. The peroxide is then precipitated by an alkali and weighed; and if lime and magnesia are present, it may be separated from those earths by the process described in the last section.

Chalybeate waters are by no means uncommon; but the most noted in Britain are those of Tunbridge, Cheltenham, and Brighton. The Bath water also contains a small quantity of iron.

4. *Sulphuretted waters*, of which the springs of Aix-la-Chapelle, Harrowgate, and Moffat afford examples, contain hydrosulphuric acid, and are easily recognized by their odour, and by causing a brown precipitate with a salt of lead or silver. The gas is readily expelled by boiling, and its quantity may be inferred by transmitting it through a solution of acetate of oxide of lead, and weighing the sulphuret which is generated.

5. Those mineral springs are called *saline*, the character of which is caused by saline compounds. The salts which are most frequently contained in these waters are the sulphates and carbonates of lime, magnesia, and soda, and the chlorides of calcium, magnesium, and sodium. Potassa sometimes exists in them, and Berzelius has found lithia in the spring of Carlsbad. It has lately been discovered that the presence of hydriodic acid in small quantity is not unfrequent.[*] As examples of saline water may be enumerated the springs of Epsom, Cheltenham, Bath, Bristol, Barèges, Buxton, Pitcaithly, and Toeplitz.

The first object in examining a saline spring is to determine the nature of its ingredients. Hydrochloric acid is detected by nitrate of oxide of silver, and sulphuric acid by chloride of barium; and if an alkaline carbonate be present, the precipitate occasioned by either of these tests will contain a carbonate of oxide of silver or baryta. The presence of lime and magnesia may be discovered, the former by oxalate of ammonia, and the latter by phosphate of ammonia. Potassa is known by the action of chloride of platinum (page 297). To detect soda, the water should be evaporated to dryness, the deliquescent salts removed by alcohol, and the matter insoluble in that menstruum taken up by a small quantity of water, and allowed to crystallize by spontaneous evaporation. The salt of soda may then be recognized by the rich yellow colour which it communicates to flame (page 302). If the presence of hydriodic acid be suspected, the solution is brought to dryness, the soluble parts dissolved in two or three drachms of a cold solution of starch, and strong sulphuric acid gradually added (page 229).

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[*] The salt spring at Theodorshalle, in Germany, contains a considerable quantity of bromine. See note, page 233.—*Ed.*

Having thus ascertained the nature of the saline ingredients, their quantity may be determined by evaporating a pint of water to dryness, heating to low redness, and weighing the residue. In order to make an exact analysis, a given quantity of the mineral water is concentrated in an evaporating basin as far as can be done without causing either precipitation or crystallization, and the residual liquid is divided into two equal parts. From one portion the sulphuric and carbonic acids are thrown down by nitrate of baryta, and after collecting the precipitate on a filter, the hydrochloric acid is precipitated by nitrate of oxide of silver. The mixed sulphate and carbonate is exposed to a low red heat, and weighed; and the latter is then dissolved by dilute hydrochloric acid, and its quantity determined by weighing the sulphate. The chloride of silver, of which 143.42 parts correspond to 36.42 of hydrochloric acid, is fused in a platinum spoon or crucible, in order to render it quite free from moisture. To the other half of the concentrated mineral water, oxalate of ammonia is added for the purpose of precipitating the lime; and the magnesia is afterwards thrown down as the ammoniaco-phosphate, by means of ammonia and phosphoric acid. Having thus determined the weight of each of the fixed ingredients excepting the soda, the loss of course gives the quantity of that alkali; or it may be procured in a separate state by the process described in the foregoing section.

The individual constituents of the water being known, it remains to determine the state in which they were originally combined. In a mineral water containing sulphuric and hydrochloric acids, lime, and soda, it is obvious that three cases are possible. The liquid may contain sulphate of lime and chloride of sodium, or chloride of calcium and sulphate of soda; or each acid may be distributed between both the bases. It was at one time supposed that the lime must be in combination with sulphuric acid, because the sulphate of that earth is left when the water is evaporated to dryness. This, however, by no means follows. In whatever state the lime may exist in the original spring, gypsum will be generated as soon as the concentration reaches that degree at which sulphate of lime cannot be held in solution. The late Dr. Murray, who treated this question with much sagacity, observes that some mineral waters, which contain the four principles above mentioned, possess higher medicinal virtues than can be justly ascribed to the presence of sulphate of lime. He advances the opinion that alkaline bases are united in mineral waters with those acids with which they form the most soluble compounds, and that the insoluble salts obtained by evaporation are merely products. He, therefore, proposes to arrange the substances determined by analysis according to this supposition. (Edin. Phil. Trans. vii.) To this practice there is no objection; but it is probable that each acid is rather distributed between several bases than combined exclusively with either (page 129).

Sea-water may be regarded as one of the saline mineral waters. Its taste is disagreeably bitter and saline, and its fixed constituents amount to about three per cent. Its specific gravity varies from 1.0269 to 1.0285; and it freezes at about 28.5° F. According to the analysis of Dr. Murray, 10,000 parts of water from the Frith of Forth contain 220.01 parts of common salt, 33.16 of sulphate of soda, 42.08 of muriate of magnesia, and 7.84 of muriate of lime. Wollaston detected potassa in sea-water, which likewise contains small quantities of hydriodic and hydrobromic acids.

The water of the Dead Sea has a far stronger saline impregnation than sea-water, containing one-fourth of its weight of solid matter. It has a peculiarly bitter, saline, and pungent taste, and its specific gravity is 1.211. According to the analysis of Marcet, 100 parts of it are composed of muriate of magnesia 10.246, muriate of soda 10.36, muriate of lime 3.92, and sulphate of lime 0.054. In the river Jordan, which flows into the Dead Sea, Marcet discovered the same principles as in the lake itself.

6. *Siliceous waters* are very rare, and in those hitherto discovered, the silica appears to have been dissolved by means of soda. The most remarkable of these are the boiling springs of the Geyser and Rykum in Iceland, a gallon of which, according to the analysis of Black, contains the following substances: (Edinburgh Philos. Trans. iii. 95.)

	Geyser.	Rykum.
Soda	5.56	3
Alumina	2.8	0.29
Silica	31.5	21.83
Muriate of soda	14.42	16.96
Sulphate of soda	8.57	7.53

The hot springs of Pinnarkoon and Loorgootha in India are analogous to the foregoing. A gallon of the water yields about 24 grains of solid matter; and the saline contents, sent to Dr. Brewster by Mr. P. Breton, I found to contain 21.5 per cent. of silica, 19 of chloride of sodium, 19 of sulphate of soda, 19 of carbonate of soda, pure soda 5, and 15.5 of water. (Edinburgh Journal of Science, No. xvii. p. 97.)

It is remarkable that nitrogen gas very generally occurs in hot springs. It was found by Longchamp in various hot springs of France, and a similar observation has been made by Dr. Daubeny. Its probable source is clearly referable to atmospheric air contained in water, which air has been deprived of its oxygen by chemical changes in the interior of the earth.

TABLE

Showing the Composition of several of the Principal Mineral Waters.
(From Dr. Henry's Elements.)

[N. B. The temperature, when not expressed, is to be understood to be 49° or 50° Fahrenheit.]

I. Carbonated Waters.

Seltzer. Bergmann.

In each wine pint.

Carbonic acid	17 cub. in.

Specific gravity 1.0027.

Carbonate of soda	4 grs.
——— of magnesia . .	5
——— of lime	3
Chloride of sodium	17
	29

Carlsbad. (Temperature 165° F.) Berzelius.

In a wine pint.

Carbonic acid	5 cub. in.

In 1000 parts by weight.

Sulphate of soda . .	2.58714 grs.
Carbonate of soda . .	1.25200
Chloride of sodium .	1.04893
Carbonate of lime . .	0.31219
Fluate of do. . . .	0.00331
Phosphate of do. . .	0.00019
Carbonate of strontia .	0.00097
——— of magnesia	0.18221
Phosphate of alumina	0.00034
Carbonate of iron . .	0.00424
——— of manganese, a trace	
Silica	0.07504
	5.46656

Spa. Bergmann.

Specific gravity 1.0010.

In each wine pint.

Carbonic acid	13 cub. in.

Carbonate of soda . . .	1.5 grs.
——— of magnesia .	4.5
——— of lime . . .	1.5
Chloride of sodium . . .	0.2
Oxide of iron	0.6
	8.3

Pyrmont. Bergmann.

Specific gravity 1.0024.

In each wine pint.

Carbonic acid	26 cub. in.

Carbonate of magnesia .	10 grs.
——— of lime . . .	4.5
Sulphate of magnesia .	5.5
——— of lime . . .	8.5
Chloride of sodium . .	1.5
Oxide of iron	0.6
	30.6

Pougues. Hassenfratz.

In each wine pint.

Carbonic acid	30 cub. in.

Carbonate of soda . . .	10 grs.
——— of magnesia .	1.2
——— of lime . . .	12
Chloride of sodium . .	2.2
Oxide of iron	2.5
Silica	0.5
	28.4

II. Sulphuretted Waters.

Aix-la-Chapelle. Bergmann.

Temperature 143°.

In each wine pint.

Sulphuretted hydrogen	5.5	cub. in.
Carbonate of soda	12	grs.
——— of lime	4.75	
Muriate of soda	5	
	21.75	

Cheltenham, Sulphur Spring.

Brande and Parkes.

Specific gravity 1.0085.

In each wine pint.

Carbonic acid	1.5	cub. in.
Sulphuretted hydrogen	2.5	
Sulphate of soda	23.5	grs.
——— of magnesia	5	
——— of lime	1.2	
Muriate of soda	35	
Oxide of iron	0.3	
	65	

Leamington, Sulphur Water.

Scudamore.

Specific gravity 1.0042.

Sulphuretted hydrogen, quantity not ascertained.

In each pint.

Muriate of soda	15	grs.
——— of lime	7.96	
——— of magnesia	3.30	
Sulphate of soda	11.60	
Oxide of iron	a trace	
	37.86	

Moffat. Garnet.

Nitrogen	0.5	cub. in.
Carbonic acid	0.6	
Sulphuretted hydrogen	1.2	
Muriate of soda	4.5	grs.

Harrowgate Water.

New Well, at the Crown Inn.

(West. Quart. Journ. xv. 82.)

Specific gravity 1.01286 at 69°.

One wine gallon contains

Sulphuretted hydrogen	6.4	cub. in.
Carbonic acid	5.25	
Azote	6.5	
Carburetted hydrogen	4.65	
	22.8	

Also,

Muriate of soda	735	grs.
——— of lime	71.5	
——— of magnesia	43	
Bicarbonate of soda	14.75	
	864.25	

Old Well.

Sp. gr. 1.01324 at 60°.

Sulphuretted hydrogen	14	cub. in.
Carbonic acid	4.25	
Azotic gas	8	
Carburetted hydrogen	4.15	
	30.4	

Also,

Muriate of soda	752	grs.
——— of lime	65.75	
——— of magnesia	29.2	
Bicarbonate of soda	12.8	
	859.75	

III. Saline Waters.

Seidlitz. Bergmann.

Specific gravity 1.0060.

In a pint.

Carbonate of magnesia	2.5	grs.
——— of lime	0.8	
Sulphate of magnesia	180	
——— of lime	5	
Muriate of magnesia	4.5	
	192.8	

Cheltenham, pure saline.

Parkes and Brande.

In each pint.

Sulphate of soda	15	grs.
——— of magnesia	11	
——— of lime	4.5	
Muriate of soda	50	
	80.5	

LEAMINGTON, saline. Scudamore.

Specific gravity 1.0119.

In a pint.

Muriate of soda	53.75 grs.
——— of lime	28.64
——— of magnesia .	20.16
Sulphate of soda	7.83
Oxide of iron	a trace
	110.38

LEAMINGTON, Lord Aylesford's Spring. Scudamore.

Specific gravity 1.0093.

In a pint.

Muriate of soda	12.25 grs.
——— of lime	28.24
——— of magnesia .	5.22
Sulphate of soda	32.96
Oxide of iron	a trace
	78.67

BRISTOL. Carrick.

Temp. 74°. Sp. gravity 1.00077.

In each pint.

Carbonic acid . . .	3.5 cub. in.
Carbonate of lime	1.5 grs.
Sulphate of soda	1.5
——— of lime	1.5
Muriate of soda	0.5
——— of magnesia . . .	1
	6

BATH. Phillips.

Temp. 109° to 117°. Sp. gr. 1.002.

In each pint.

Carbonic acid . . .	1.2 cub. in.
Carbonate of lime	0.8 grs.
Sulphate of soda	1.4
——— of lime	9.3
Muriate of soda	3.4
Silica	0.2
Oxide of iron	a trace
	15.1

BATH. Solid contents. Scudamore.

Muriate of lime	1.2 grs.
——— of magnesia .	1.6
Sulphate of lime	9.5
——— of soda	0.9
Silica	0.2
Oxide of iron	0.01985
Loss, partly carb. of soda	0.58015
	14

Mr. Cuff has found both potassa and iodine in the Bath waters.

BUXTON. Scudamore.

Sp. gr. at 60° 1.0006. Temp. 82°.

In a wine gallon.

Carbonic acid	1.5 cub. in.
Nitrogen	4.64
Muriate of magnesia . .	0.58 grs.
——— of soda	2.40
Sulphate of lime . . .	0.60
Carbonate of lime . . .	10.40
Extractive and vegetable matter	0.50
Loss	0.52
	15

Or, according to Dr. Murray's views.

Sulphate of soda . . .	0.63 grs.
Muriate of lime . . .	0.57
——— of soda	1.80
——— of magnesia . .	0.58
Carbonate of lime . . .	10.40
Extract and loss . . .	1.02
	15

MATLOCK BATH. Scudamore.

Temp. 68°. Sp. gr. 1.0003.

Free carbonic acid.
Muriates and sulphates of } magnesia, lime, and soda?
in very minute quantities not yet ascertained.

IV. Chalybeate Waters.

Tunbridge. Scudamore.

Specific gravity 1.0007.

In each gallon.

Muriate of soda . . .	2.46 grs.
——— of lime	0.39
——— of magnesia . .	0.29
Sulphate of lime . . .	1.41
Carbonate of lime . . .	0.27
Oxide of iron	2.22
Traces of manganese, vegetable fibre, silica, &c.	0.44
Loss	0.13
	7.61

Cheltenham. Brande and Parkes.

Specific gravity 1.0092.

In a pint.

Carbonic acid	2.5 cub. in.
Carbonate of soda . . .	0.5 grs.
Sulphate of soda	22.7
——— of magnesia . .	6
——— of lime	2.5
Muriate of soda	41.3
Oxide of iron	0.8
	73.8

Brighton. Marcet.

Specific gravity 1.00108.

Carbonic acid gas . .	2½ cub. in.
Sulphate of iron . . .	1.80 grs.
——— of lime . . .	4.09
Muriate of soda . . .	1.53
——— of magnesia . .	0.75
Silica	0.14
Loss	0.19
	8.5

Harrowgate, Oddie's Chalybeate.

Scudamore.

Specific gravity 1.0053.

In each gallon.

Muriate of soda . . .	300.4 grs.
——— of lime . . .	22
——— of magnesia .	9.9
Sulphate of lime . . .	1.86
Carbonate of do. . . .	6.7
——— of magnesia .	0.8
Oxide of iron	2.4
Residue, chiefly silica .	4
	344.46

APPENDIX.

I AM indebted to Mr. Graham for the following interesting communication on certain hydrated salts and peroxides, and on phosphuretted hydrogen.

Various classes of salts, besides the arseniates and phosphates, contain water which is essential to their constitution, of which the sulphates of magnesia, and the protoxides of zinc, manganese, iron, copper, nickel, and cobalt are examples. These salts crystallize from their aqueous solution either with seven or five equivalents of water (page 435), one of which is in a state of much more intimate union than the other six or four. Thus, crystallized sulphate of oxide of zinc loses six eq. of water at a temperature not exceeding 65° when placed over sulphuric acid in vacuo, but retains one eq. of water at 410°, and all inferior temperatures. The salt may be viewed as a sulphate of oxide of zinc and water, with six eq. of water of crystallization; a constitution which may be expressed as follows, $\dot{H}\dot{Z}n\dddot{S}+6\dot{H}$. This sulphate of zinc may be made anhydrous, but when moistened always regains one eq. of water, slaking with the evolution of heat. This last equivalent of water appears to discharge a basic function in the constitution of the salt, and affords a clue to the disposition of this sulphate to form double sulphates. Sulphate of oxide of zinc combines with sulphate of potassa, and forms a well-known double salt (page 441), in which the basic water of the sulphate of zinc is replaced by sulphate of potassa without any farther change. The formula of the double sulphate is $(\dot{K}\dddot{S})\dot{Z}n\dddot{S}+6\dot{H}$. In the double salt, the whole six eq. of water are retained with somewhat greater force than in the simple sulphate, but even the double salt becomes anhydrous below 212° in vacuo.

The sulphates of the other metallic oxides mentioned are quite analogous to sulphate of oxide of zinc in their habitudes with water, although the particular temperature at which they part with their water of crystallization is different in each. The analogy holds also in the double sulphates of those oxides.

Of hydrous sulphate of lime or gypsum, the two eq. of water which it contains appear to be essential, and are retained at 212°. At a temperature not exceeding 270°, this salt becomes anhydrous, but retains the power of recombining with two eq. of water or setting. The salt is then in a peculiar condition. Heated above 300° the salt becomes properly sulphate of lime, and has lost the disposition to combine with water.

Berzelius found the peroxide of tin formed by the action of nitric acid on metallic tin to differ in certain properties from the same compound precipitated from a persalt of tin by an alkali, and distinguished the first under the name of the nitric acid peroxide of tin. Both peroxides combine with hydrochloric acid, but the hydrochlorate of the nitric acid peroxide is peculiar in being insoluble in water strongly acidulated with hydrochloric acid. The precipitated peroxide of tin assumes all the properties of the other modification when kept for some time in boiling water, or even when strongly dried over sulphuric acid in vacuo at the ordinary temperature of the atmosphere.

The two modifications are merely different hydrates of the peroxide of tin, but it is difficult to ascertain what proportion of water is essential to each. The hydrates combine with acids and form two sets of compounds; but absolute peroxide of tin itself (which is obtained by heating the hydrated peroxide to redness) has no disposition to combine with acids.

Rose has shown that the two kinds of phosphuretted hydrogen, one of which is spontaneously inflammable in air, and the other not so, are of the same composition and specific gravity. To account for their possessing different properties recourse is had to the doctrine of isomerism. But the observations of Graham indicate the existence of a *peculiar principle* in the spontaneously inflammable species, which principle may be withdrawn, and leaves the gas not spontaneously inflammable.

1. The peculiar principle is withdrawn by *charcoal*, which has been heated to redness and cooled under mercury, in the proportion of 1-500dth part of the volume of the gas, with a contraction of not more than 1 per cent., the greater part of which is due to the absorption of a portion of the gas itself by the charcoal. Baked clay has a similar effect upon the gas. The peculiar principle appears to be present in a small, almost infinitesimal proportion, and cannot be separated again from the porous absorbent by which it has been taken up.

2. The vapours of essential oils, of naphtha, and of ether, olefiant gas, and the other carburets of hydrogen, destroy the peculiar principle in a short time, or prevent its action.

3. Concentrated phosphorous and phosphoric acids withdraw the peculiar principle; so does arsenic acid, but the last quickly reacts on the phosphuretted hydrogen itself. A little air destroys the inflammability of a large quantity of gas, probably from the phosphoric acid which is produced.

4. A most minute quantity of potassium or of the amalgam of potassium destroys the spontaneous inflammability without occasioning any reduction of volume that could be measured. Caustic potassa has not this effect.

The property of taking fire spontaneously in air may be communicated to phosphuretted hydrogen, which does not possess it, by a very slight impregnation of nitrous acid vapour. The quantity of nitrous acid vapour should not much exceed 1 measure to 1000 measures of the gas: when the proportion of nitrous acid is greater, the mixture is not spontaneously inflammable, but becomes so on diluting it with phosphuretted hydrogen. The gas continues spontaneously inflammable for 24 or 48 hours over water, but for a shorter period when kept over mercury. Pure nitric oxide impedes the oxidation of phosphuretted hydrogen, and cannot be substituted for the nitrous acid. The addition of nitrous acid to the phosphuretted hydrogen may be made in various ways. Commercial sulphuric acid, diluted with three volumes of water and cooled, contains nitrous acid, which it imparts to phosphuretted hydrogen agitated in a phial along with it. Hence, too, the hydrogen gas evolved at the beginning of the action of sulphuric acid upon zinc, often suffices for making phosphuretted hydrogen inflammable, when added to the extent of half a volume. The nitrous acid of Dulong may be added directly to phosphuretted hydrogen over mercury by passing it up in a glass spherule. The most convenient process, however, is to impregnate hydrogen gas first with nitrous acid. For that purpose, to a three-ounce phial add a drachm of nitric acid with a few drops of the nitrous acid of Dulong. Fill up the phial with water, and make use of it as a receiver to collect hydrogen gas. The addition to phosphuretted hydrogen of $\frac{1}{4}$th or $\frac{1}{6}$th of its volume of this nitrous hydrogen, does not disturb the transparency of that gas, but renders it highly inflammable. A greater proportion of the nitrous hydrogen is generally injurious.

Now, phosphuretted hydrogen made inflammable in this way has a great analogy to the gas procured at first in a spontaneously inflammable state by the common processes. The factitious gas is deprived of its spontaneous inflammability by porous absorbents, by carburets of hydrogen, by amalgam of potassium, but not by phosphoric acid. Neither gas can be kept over mercury for a long period without losing its spontaneous inflammability.

It seems probable, from the action of potassium and the carburets of hydrogen on the ordinary spontaneously inflammable gas, that its peculiar principle is an oxygenated body. It cannot be nitrous acid, but it may be a compound of phosphorus and oxygen, $\underline{\ddot{\mathrm{P}}}$, analogous to nitrous acid. In all the reactions by which the spontaneously inflammable phosphuretted hydrogen is produced, we have the formation of compounds of phosphorus and oxygen, such as hypophosphorous and phosphoric acids. The compound $\underline{\ddot{\mathrm{P}}}$ is hypothetic, however, and has not been formed directly, although the complete analogy between phosphuretted hydrogen and ammonia affords a presumptive argument of its possible existence.

Nitrous, or rather hyponitrous, acid has a disposition to unite with other acids. It may, therefore, promote the oxidability of phosphuretted hydrogen in air, by uniting with the resulting acid compound of phosphorus and oxygen; but this is a mere conjecture.

TABLE I.

TABLE of the elastic Force of Aqueous Vapour at different Temperatures, expressed in Inches of Mercury.

Temp. Fahr.	Force of Vapour.		Temp. Fahr.	Force of Vapour.		Temp. Fahr.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
32°	0.200	0.200	79°	0.971		126°	3.89	
33	0.207		80	1.00	1.010	127	4.00	
34	0.214		81	1.04		128	4.11	
35	0.221		82	1.07		129	4.22	
36	0.229		83	1.10		130	4.34	4 366
37	0.237		84	1.14		131	4.47	
38	0.245		85	1.17	1.170	132	4.60	
39	0.254		86	1.21		133	4.73	
40	0.263	0.250	87	1.24		134	4.86	
41	0.273		88	1.28		135	5.00	5.070
42	0.283		89	1.32		136	5.14	
43	0.294		90	1.36	1,360	137	5.29	
44	0.305		91	1.40		138	5.44	
45	0.316		92	1.44		139	5.59	
46	0.328		93	1.48		140	5.74	5.770
47	0.339		94	1.53		141	5.90	
48	0.351		95	1.58	1.640	142	6.05	
49	0.363		96	1.63		143	6.21	
50	0.375	0.360	97	1.68		144	6.37	
51	0.388		98	1.74		145	6.53	6.600
52	0.401		99	1.80		146	6.70	
53	0.415		100	1.86	1.860	147	6.87	
54	0.429		101	1.92		148	7.05	
55	0.443	0.416	102	1.98		149	7.23	
56	0.458		103	2.04		150	7.42	7.530
57	0.474		104	2.11		151	7.61	
58	0.490		105	2.18	2.100	152	7.81	
59	0.507		106	2.25		153	8.01	
60	0.524	0.516	107	2.32		154	8.20	
61	0.542		108	2.39		155	8.40	8.500
62	0.560		109	2.46		156	8.60	
63	0.578		110	2.53	2.456	157	8.81	
64	0.597		111	2.60		158	9.02	
65	0.616	0.630	112	2.68		159	9,24	
66	0.635		113	2.76		160	9.46	9.600
67	0.655		114	2.84		161	9.68	
68	0.676		115	2.92	2.820	162	9.91	
69	0.698		116	3,00		163	10.15	
70	0.721	0.726	117	3.08		164	10.41	
71	0.745		118	3.16		165	10.68	10.800
72	0.770		119	3.25		166	10.96	
73	0.796		120	3.33	2.300	167	11.25	
74	0.823		121	3.42		168	11.54	
75	0.851	0.860	122	3.50		169	11.83	
76	0.880		123	3.59		170	12.13	12.050
77	0.910		124	3.69		171	12.43	
78	0.940		125	3.79	3.830	172	12.73	

Table I. continued.

Temp. Fahr.	Force of Vapour.		Temp. Fahr.	Force of Vapour.		Temp. Fahr.	Force of Vapour.	
	Dalton.	Ure.		Dalton.	Ure.		Dalton.	Ure.
173°	13.02		224°	37.53		275°	83.13	93.480
174	13.32		225	38.20	39.110	276	84.35	
175	13 62	13.550	226	38.89	40.100	277	85.47	97.800
176	13.92		227	39.59		278	86.50	
177	14.22		228	40.30		279	87.63	101.600
178	14.52		229	41.02		280	88.75	101.900
179	14.83		230	41·75	43.100	281	89.87	104.400
180	15.15	15.160	231	42·49		282	90.99	
181	15.50		232	43·24		283	92.11	107.700
182	15.86		233	44·00		284	93.23	
183	16.23		234	44·78	46 800	285	94.35	112.200
184	16.61		235	45·58	47.220	286	95.48	
185	17.00	16.900	236	46·39		287	96.64	114.800
186	17.40		237	47·20		288	97.80	
187	17.80		238	48·02	50.300	289	98.96	118.200
188	18.20		239	48·84		290	100.12	120.150
189	18.60		240	49·67	51.700	291	101.28	
190	19.00	19.000	241	50.50		292	102.45	123.100
191	19.42		242	51.34	53.600	293	103.63	
192	19.86		243	52.18		294	104.80	126.700
193	20.32		244	53.03		295	105.97	129.000
194	20.77		245	53.88	56.340	296	107.14	
195	21.22	21.100	246	54.68		297	108.31	133.900
196	21.68		247	55.54		298	109.48	137.400
197	22.13		248	56.42	60.400	299	110.64	
198	22.69		249	57.31		300	111.81	139.700
199	23.16		250	58.21	61.900	301	112.98	
200	23.64	23.600	251	59.12	63.500	302	114.15	144.300
201	24.12		252	60.05		303	115.32	147.700
202	24.61		253	61.00		304	116.50	
203	25.10		254	61.92	66.700	305	117.68	150.560
204	25.61		255	62.85	67.25	306	118.86	154.400
205	26.13	25.900	256	63.76		307	120.03	
206	26.66		257	64.82	69.800	308	121.20	157.700
207	27.20		258	65.78		309	122.37	
208	27.74		259	66.75		310	123.53	161.300
209	28.29		260	67.73	72.300	311	124.69	164.800
210	28.84	28.880	261	68.72		312	125.85	167.000
211	29.41		262	69.72	75.900	313	127.00	
212	30.00	30.000	263	70.73		314	128.15	
213	30·60		264	71.74	77.900	315	129.29	
214	31.21		265	72.76	78.040	316	130.43	
215	31.83		266	73.77		317	131.57	
216	32.46	33.400	267	74.79	81.900	318	132.72	
217	33.09		268	75.80		319	133.86	
218	33.72		269	76.82	84.900	320	135.00	
219	34·35		270	77.85	86.300	321	136.14	
220	34.99	35.540	271	78.89	88.000	322	137.28	
221	35.63	36.700	272	79.94		323	138.42	
222	36.25		273	80.98	91.200	324	139.56	
223	36.88		274	82.01		325	140.70	

TABLE II.

Dr. Ure's TABLE, showing the elastic Force of the Vapours of Alcohol, Ether, Oil of Turpentine, and Petroleum or Naphtha, at different Temperatures, expressed in Inches of Mercury.

Ether.	
Temp.	Force of Vapour.
34°	6.20
44	8.10
54	10.30
64	10.00
74	16.10
84	20.00
94	24.70
104	30.00
105	30.00
110	32.54
115	35.90
120	39.47
125	43.24
130	47.14
135	51.90
140	56.90
145	62.10
150	67.60
155	73.60
160	80.30
165	86.40
170	92.80
175	99.10
180	108.30
185	116.10
190	124.80
195	133.70
200	142.80
205	151.30
210	166.00

Alcohol sp. gr. 0.813.	
Temp.	Force of Vapour.
32°	0.40
40	0.56
45	0.70
50	0.86
55	1.00
60	1.23
65	1.49
70	1.76
75	2.10
80	2.45
85	2.93
90	3.40
95	3.90
100	4.50
105	5.20
110	6.00
115	7.10
120	8.10
125	9.25
130	10.60
135	12.15
140	13.90
145	15.95
150	18.00
155	20.30
160	22.60
165	25.40
170	28.30
173	30.00
178.3	33.50
180	34.73
182.3	36.40
185.3	39.90
190	43.20

Alcohol sp. gr. 0.813	
Temp.	Force of Vapour.
193.3°	46.60
196.3	50.10
200	53.00
206	60.10
210	65.00
214	69.30
216	72.20
220	78.50
225	87.50
230	94.10
232	97.10
236	103.60
238	106.90
240	111.24
244	118.20
247	122.10
248	126.10
249.7	131.40
250	132.30
252	138.60
254.3	143.70
258.6	151.60
260	155.20
262	161.40
264	166.10

Petroleum.	
Temp.	Force of Vapour.
316°	30.00
320	31.70
325	34.00
330	36.40
335	38.90
340	41.60
345	44.10
350	46.86
355	50.20
360	53.30
365	56.90
370	60.70
372	61.90
375	64.00

Oil of Turpentine.	
Temp.	Force of Vapour.
304°	30.00
307.6	32.60
310	33.50
315	35.20
320	37.06
322	37.80
326	40.20
330	42.10
336	45.00
340	47.30
343	49.40
347	51.70
350	53.80
354	56.60
357	58.70
360	60.80
362	62.40

TABLE III.

Dr. Ure's TABLE of the Quantity of Oil of Vitriol, of sp. gr. 1.8485, *and of Anhydrous Acid, in* 100 *Parts of dilute Sulphuric Acid, at different Densities.*

Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.	Liquid.	Sp. Gr.	Dry.
100	1.8485	81.54	66	1.5503	53.82	32	1.2334	26.09
99	1.8475	80.72	65	1.5390	53.00	31	1.2260	25.28
98	1.8460	79.90	64	1.5280	52.18	30	1.2184	24.46
97	1.8439	79.09	63	1.5170	51.37	29	1.2108	23.65
96	1.8410	78.28	62	1.5066	50.55	28	1.2032	22.83
95	1.8376	77.46	61	1.4960	49.74	27	1.1956	22.01
94	1.8336	76.65	60	1.4860	48.92	26	1.1876	21.20
93	1.8290	75.83	59	1.4760	48.11	25	1.1792	20.38
92	1.8233	75.02	58	1.4660	47.29	24	1.1706	19.57
91	1.8179	74.20	57	1.4560	46.48	23	1.1626	18.75
90	1.8115	73.39	56	1.4460	45.66	22	1.1549	17.94
89	1.8043	72.57	55	1.4360	44 85	21	1.1480	17.12
88	1.7962	71.75	54	1.4265	44.03	20	1.1410	16.31
87	1.7870	70.94	53	1.4170	43.22	19	1.1330	15.49
86	1.7774	70.12	52	1.4073	42.40	18	1.1246	14.68
85	1.7673	69.31	51	1.3977	41.58	17	1.1165	13.86
84	1.7570	68.49	50	1.3884	40.77	16	1.1090	13.05
83	1.7465	67.68	49	1.3788	39.95	15	1.1019	12.23
82	1.7360	66.86	48	1.3697	39.14	14	1.0953	11.41
81	1.7245	66.05	47	1.3612	38.32	13	1.0887	10.60
80	1.7120	65.23	46	1·3530	37.51	12	1.0809	9.78
79	1.6993	64.42	45	1.3440	36.69	11	1.0743	8.97
78	1.6870	63.60	44	1.3345	35.88	10	1.0682	8.15
77	1.6750	62.78	43	1.3255	35.06	9	1.0614	7.34
76	1.6630	61.97	42	1.3165	34.25	8	1.0544	6.52
75	1.6520	61.15	41	1.3080	33.43	7	1.0477	5.71
74	1·6415	60.34	40	1·2999	32.61	6	1.0405	4.89
73	1.6321	59.52	39	1·2913	31.80	5	1.0336	4.08
72	1.6204	58.71	38	1·2826	30.98	4	1.0268	3.26
71	1.6090	57.89	37	1·2740	30.17	3	1.0206	2.446
70	1.5975	57.08	36	1·2654	29.35	2	1.0140	1.63
69	1.5868	56.26	35	1·2572	28.54	1	1.0074	0.8154
68	1.5760	55.45	34	1·2490	27.72			
67	1.5648	54.63	33	1·2409	26·91			

TABLE IV.

Dr. Ure's TABLE of the Quantity of Real or Anhydrous Nitric Acid in 100 Parts of Liquid Acid, at different Densities.

Specific Gravity.	Real Acid in 100 parts of the liquid.	Specific Gravity.	Real Acid in 100 parts of the liquid.	Specific Gravity.	Real Acid in 100 parts of the liquid.
1.5000	79.700	1.3783	52.602	1.1895	26.301
1.4980	78.903	1.3732	51.805	1.1833	25.504
1.4960	78.106	1.3681	51.068	1.1770	24.707
1.4940	77.309	1.3630	50.211	1.1709	23.910
1.4910	76.512	1.3579	49.414	1.1648	23.113
1.4880	75.715	1.3529	48.617	1.1587	22.316
1.4850	74.918	1.3477	47.820	1.1526	21.519
1.4820	74.121	1.3427	47.023	1.1465	20.722
1.4790	73.324	1.3376	46.226	1.1403	19.925
1.4760	72.527	1.3323	45.429	1.1345	19.128
1.4730	71.730	1.3270	44.632	1.1286	18.331
1.4700	70.933	1.3216	43.835	1.1227	17.534
1.4670	70.136	1.3163	43.038	1.1168	16.737
1.4640	69.339	1.3110	42.241	1.1109	15.940
1.4600	68.542	1.3056	41.444	1.1051	15.143
1.4570	67.745	1.3001	40.647	1.0993	14.346
1.4530	66.948	1.2947	39.850	1.0935	13.549
1.4500	66.155	1.2887	39.053	1.0878	12.752
1.4460	65.354	1.2826	38.256	1.0821	11,955
1.4424	64.557	1.2765	37.459	1.0764	11.158
1.4385	63.760	1.2705	36.662	1.0708	10.361
1.4346	62.963	1.2644	35.865	1.0651	9.564
1.4306	62.166	1.2583	35.068	1.0595	8.767
1.4269	61.369	1.2523	34.271	1.0540	7.970
1.4228	60.572	1.2462	33.474	1.0485	7.173
1.4189	59.775	1.2402	32.677	1.0430	6.376
1.4147	58.978	1.2341	31,880	1.0375	5.579
1.4107	58.181	1.2277	31.083	1.0320	4.782
1.4065	57.384	1.2212	30.286	1.0267	3.985
1.4023	56.587	1.2148	29.489	1.0212	3.188
1.3978	55.790	1.2084	28.692	1.0159	2.391
1.3945	54.993	1.2019	27.895	1.0106	1.594
1.3882	54.196	1.1958	27.098	1.0053	0.797
1.3833	53.399				

TABLE V.

TABLE of Lowitz showing the Quantity of Absolute Alcohol in Spirits of different Specific Gravities.

100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.		100 Parts.		Sp. Gravity.	
Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.	Alc.	Wat.	At 68°.	At 60°.
100	0	0.791	0.796	66	34	0.877	0.881	32	68	0.952	0.955
99	1	0.794	0.798	65	35	0.880	0.883	31	69	0.954	0.957
98	2	0.797	0.801	64	36	0.882	0.886	30	70	0.956	0.958
97	3	0.800	0.804	63	37	0.885	0.889	29	71	0.957	0.960
96	4	0.803	0.807	62	38	0.887	0.891	28	72	0.959	0.962
95	5	0.805	0.809	61	39	0.889	0.893	27	73	0.961	0.963
94	6	0.808	0.812	60	40	0.892	0.896	26	74	0.963	0.965
93	7	0.811	0.815	59	41	0.894	0.898	25	75	0.965	0.967
92	8	0.813	0.817	58	42	0.896	0.900	24	76	0.966	0.968
91	9	0.816	0.820	57	43	0.899	0.902	23	77	0.968	0.970
90	10	0.818	0.822	56	44	0.901	0.904	22	78	0.970	0.972
89	11	0.821	0.825	55	45	0.903	0.906	21	79	0.971	0.973
88	12	0.823	0.827	54	46	0.905	0.908	20	80	0.973	0.974
87	13	0.826	0.830	53	47	0.907	0.910	19	81	0.974	0.975
86	14	0.828	0.832	52	48	0.909	0.912	18	82	0.976	0.977
85	15	0.831	0.835	51	49	0.912	0.915	17	83	0.977	0.978
84	16	0.834	0.838	50	50	0.914	0.917	16	84	0.978	0.979
83	17	0.836	0.840	49	51	0.917	0.920	15	85	0.980	0.981
82	18	0.839	0.843	48	52	0.919	0.922	14	86	0.981	0.982
81	19	0.842	0.846	47	53	0.921	0.924	13	87	0.983	0.984
80	20	0.844	0.848	46	54	0.923	0.926	12	88	0.985	0.986
79	21	0.847	0.851	45	55	0.925	0.928	11	89	0.986	0.987
78	22	0.849	0.853	44	56	0.927	0.930	10	90	0.987	0.988
77	23	0.851	0.855	43	57	0.930	0.933	9	91	0.988	0.989
76	24	0.853	0.857	42	58	0.932	0.935	8	92	0.989	0.990
75	25	0.856	0.860	41	59	0.934	0.937	7	93	0.991	0.991
74	26	0.859	0.863	40	60	0.936	0.939	6	94	0.992	0.992
73	27	0.861	0.865	39	61	0.938	0.941	5	95	0.994	
72	28	0.863	0.867	38	62	0.940	0.943	4	96	0.995	
71	29	0.866	0.870	37	63	0.942	0.945	3	97	0.997	
70	30	0.868	0.872	36	64	0.944	0.947	2	98	0.998	
69	31	0.870	0.874	35	65	0.946	0.949	1	99	0.999	
68	32	0.872	0.875	34	66	0.948	0.951	0	100	1.000	
67	33	0.875	0.879	33	67	0.950	0.953				

TABLE VI.

TABLE showing the Specific Gravity of Liquids, at the Temperature of 55° Fahr. corresponding to the Degrees of Baumé's Hydrometer.

For Liquids lighter than Water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10 =	1.000	17 =	.949	23 =	.909	29 =	.874	35 =	.842
11	.990	18	.942	24	.903	30	.867	36	.837
12	.985	19	.935	25	.897	31	.861	37	.832
13	.977	2	.928	26	.892	32	.856	38	.827
14	.970	21	.922	27	.886	33	.852	39	.822
15	.963	22	.915	28	.880	34	.847	40	.817
16	.955								

For Liquids heavier than Water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0 =	1.000	15 =	1.114	30 =	1.261	45 =	1.455	60 =	1.717
3	1.020	18	1.140	33	1.295	48	1.500	63	1.779
6	1.040	21	1.170	36	1.333	51	1.547	66	1.848
9	1 064	24	1.200	39	1.373	54	1.594	69	1.920
12	1.089	27	1.230	42	1.414	57	1.659	72	2.000

Mercaptan.—Professor Zeise of Copenhagen has made some interesting researches on a liquid of an ethereal character, which he terms mercaptan, from its energetic action on peroxide of mercury (corpus *mercurium captans*). When sulphovinate of baryta is distilled with a strong solution of protosulphuret of barium, a volatile liquid along with water passes over, and sulphate of baryta remains in the retort, there being no other residue when the ingredients are in atomic proportion. The ethereal product, which is formed on the surface of water, consists of two compounds, separable by careful distillation, one termed *thialic* ether (θειον sulphur), and the other mercaptan. The latter is generated in still larger quantity by the action of a sulphovinate with bisulphuret of barium, or with hydro-sulphuret of barium (page 471); but in no case is the theory of its formation complete, owing to the simultaneous production of thialic ether, the composition of which is not yet known.

Mercaptan, to judge of the facts yet ascertained, consists of hydrogen united with a compound inflammable substance, not hitherto obtained in a separate state, which Zeise calls *mercaptum* (corpus *mercurio aptum*) from its strong affinity for mercury. Like cyanogen, or bisulphuret of cyanogen, it combines with metals, hydrogen, and doubtless other elements; and these compounds are called *mercaptides* or *mercapturets*. Mercaptan is a mercapturet of hydrogen. Mercaptum consists of

Sulphur	32.2	2 eq.	. 2S
Carbon	24.48	4 eq.	. 4C
Hydrogen	5	5 eq.	. 5H
	61.68	1 eq.	$C^4H^5S^2$

Mercaptan consists of one eq. of mercaptum and one eq. of hydrogen, its symbol being $H+C^4H^5S^2$. When acted on by potassium, hydrogen gas is evolved, and mercapturet of potassium is formed. With the peroxide of mercury it acts violently, yielding water and a white crystalline solid, bimercapturet of mercury, which may be decomposed by hydrosulphuric acid, and then yields bisulphuret of mercury and mercaptan. In fact, mercaptum and mercaptan are related to each other, and apparently to many other bodies, like cyanogen and hydrocyanic acid.

Pure mercaptan is best prepared by decomposing bimercapturet of mercury with hydrosulphuric acid. It is a colourless liquid, of a highly penetrating odour, analogous to assafœtida and garlic, and of an ethereal saccharine taste. It retains its liquid form at —8°, boils at 143½°, and has a specific gravity at 59° of 0.842. It is neutral to test-paper, dissolves in ether and alcohol almost in all proportions, but is sparingly soluble in water (An. de Ch. et de Ph. lv. 87).

Mellon.—When bisulphuret of cyanogen, quite dry, is heated, a quantity of sulphur and bisulphuret of carbon are developed and expelled; while a lemon-yellow powder remains, composed of six eq. of carbon and four eq. of nitrogen. It bears a red heat without change, but at higher temperatures is resolved into pure cyanogen and nitrogen gases. It unites directly with chlorine and potassium when heated with them, and in its chemical relations appears to belong to the same class of bodies as cyanogen. It is insoluble in water and alcohol. When digested in nitric acid, it is dissolved and decomposed, being resolved, with scarcely any escape of binoxide of nitrogen, into ammonia and a new acid termed *cyanilic* acid, which crystallizes from the solution on cooling. The crystals of cyanilic acid contain 21 per cent. of water, which may be expelled by heat, and the acid itself has precisely the same composition as cyanuric acid, but its equivalent is twice as great.

Liebig, the discoverer of these compounds, has in the same essay with them (An. de Ch. et de Ph. lv. 5.) described the four following substances.

Melam.—This substance is formed by distilling dry hydrosulphocyanate of ammonia, or what amounts to the same, a mixture of sal ammoniac and sulphocyanuret of potassium. The products are ammonia, bisulphuret of carbon, hydrosulphuric acid, and melam, which remains in the retort, mixed with chloride of potassium and the excess of sal ammoniac. By levigating and washing the residue, the melam is obtained pure in the form of a yellow powder. When heated cautiously, it is resolved into mellon, ammonia, and some other volatile product. By digestion with nitric acid it yields cyanuric acid, and cyanic acid is generated when it is fused with potassa. It consists of twelve eq. of carbon, nine eq. of hydrogen, and eleven eq. of nitrogen.

Melamine.—It is generated when melam is boiled with hydrochloric acid or with a solution of pure potassa, or when mellon is boiled with that alkali, ammonia being always generated at the same time. The melamine being of sparing solubility in water, separates in colourless crystals, the form of which is a rhombic octohedron when perfect. They are insoluble in alcohol and ether.

Melamine has no alkaline reaction with test-paper, but it unites with all the acids, forming well-crystallized salts with them, and displaces ammonia and several metallic oxides from acids. Melamine is thus a remarkable instance of the artificial production of an alkaline base. It is composed of six eq. of carbon, six eq. of nitrogen, and six eq. of hydrogen, the sum of these quantities being the combining quantity of melamine.

Ammeline.—This substance is generated and held in solution by the alkali, when melam is boiled in a solution of potassa; and it is thrown down as a white precipitate when the liquid is neutralized by acetic acid. It is insoluble in water, alcohol, and ether, but is dissolved by the fixed caustic alkalies and most of the acids. It acts towards the latter as a base, though in a less distinct manner than melamine. It is composed of six eq. of carbon, five eq. of hydrogen, five eq. of nitrogen, and two eq. of oxygen.

Ammelide.—Melamine, as also melam, is resolved by strong sulphuric acid into ammelide and ammonia, and on mixing alcohol with the solution, the ammelide is thrown down as a white powder. It is also formed by boiling melamine in strong nitric acid until the solution is complete. Ammelide consists of twelve eq. of carbon, nine eq. of hydrogen, nine eq. of nitrogen, and six eq. of oxygen.

Carburetted Hydrogen in the Atmosphere.—M. Boussinghault has proved that in the air of Paris a small quantity of hydrogen, rarely amounting to 1 in 10,000 measures, is present, either free or in combination. The fact was proved by passing a large quantity of air previously dried by chloride of calcium and sulphuric acid with scrupulous care, through a red-hot tube filled with turnings of metallic copper, when a small quantity of water was always generated. This experiment he purposes repeating on the Alps. He suspects the hydrogen to be combined with carbon; because Saussure has observed that air deprived of carbonic acid gas, and then mixed with hydrogen gas and detonated, always contained traces of carbonic acid. (L'Institut, 23 August, 1834.)

Niturет of Phosphorus.—This substance is prepared by saturating the perchloride of phosphorus with dry ammoniacal gas, and then heating the product to redness in a current of dry carbonic acid gas; when hydrochlorate of ammonia, ammonia, hydrogen gas, and the vapour of phosphorus are expelled, and niturет of phosphorus remains in form of a white light powder. This compound may be heated to redness without change, and resists the action of alkaline solutions, chlorine gas, and the acids, except the concentrated nitric and sulphuric; but when fused with an alkaline hydrate, ammonia is abundantly disengaged, and a phosphate generated. Heated in the open air it slowly yields phosphoric acid. According to the analysis of H. Rose, who ascertained the preceding facts, the niturет of phosphorus consists of 15.7 parts or one eq. of phosphorus, and 14.15 parts or one eq. of nitrogen. (L'Institut, 15 February, 1834.)

Benzin.—Mitscherlich has noticed that when benzoic acid is distilled with an excess, such as 3 times its weight, of slaked lime, the acid is entirely resolved into carbonic acid, which unites with lime, and Faraday's bicarburet of hydrogen (page 251), to which Mitscherlich has given the name of benzin. The change is such that

1 eq. hydrous benzoic acid	yields	2 eq. benzin	$2(3H+6C)$
$14C+6H+4O$		and 2 eq. carbonic acid	$2(C+2O.)$

Peligot has obtained a similar result by distilling hydrated benzoate of lime; but when the anhydrous salt is used, the change is necessarily somewhat different, and a volatile liquid called *benzone* passes over, carbonate of lime remaining in the retort. In this case

1 eq. anhydrous benzoic acid	yields	1 eq. benzone	$13C+5H+O$
$14C+5H+3O$		and 1 eq. carbonic acid	$C+2O.$

By heating benzone with lime it may be deprived of all its oxygen, with production of carbonic acid and naphthaline. (L'Institut, 19 July, 1834.) These phenomena are obviously due to a play of affinities leading to the production of carbonic acid.

Mitscherlich has described, under the name of *sulpho-benzide*, a compound formed by the action of strong sulphuric acid on benzin, the reaction being such that

2 eq. benzin . . .	$2(3H+6C)$	yield	1 eq. sulpho-benzide	$5H+12C+S+2O$
and 1 eq. sulphuric acid	$S+3O$		and 1 eq. water . . .	$H+O.$

Strong nitric acid acts on benzin in a similar manner. (Mitscherlich's Lehrbuch der Chemie.)

Naphtha.—Reichenbach, of Blansko, is of opinion that native naphtha is essentially the same fluid as oil of turpentine, and contends that the former is not generated during the slow changes by which wood is converted into coal, but existed originally in the wood itself;—that, in fact, naphtha is the oil of turpentine of antediluvian pine forests. This view is founded on the close similarity in the properties of naphtha and oil of turpentine. He obtained naphtha from coal by distillation at 212°. Naphtha is certainly not generated by heat applied to beds of coal in the same manner as bituminous matter is generated during the formation of coal-gas; for native naphtha is free from the products which characterize the latter (page 549), and is quite different from coal-tar naphtha, with which it has been thought identical. (L'Institut, 7 June, 1834).

Xanthic and Hydroxanthic Acid.—When bisulphuret of carbon is agitated with a solution of pure potassa in strong alcohol, the alkalinity of the liquid disappears; and on exposing the solution to a temperature of 32°, colourless acicular crystals are deposited which acquire a yellow tint on exposure to the air. Zeise, who first prepared this salt in 1822 (Annals of Phil. N. S. iv.), supposed it to consist of potassa united with an hydracid, the radical of which he believed to be a sulphuret of carbon. To the radical of this hydracid he applied the term *xanthogen* (from ξανθος yellow, and γενναω I generate), expressive of its tendency to form yellow compounds; and to the acid he gave the name of *hydroxanthic acid*. He has since substituted the name of xanthic acid, from finding that it contains oxygen as one of its elements. He supposes it to contain the elements of one eq. of alcohol, and two eq. of bisulphuret of carbon; but its real nature has not yet been satisfactorily determined.

Xanthic acid is a colourless oily fluid, heavier than water, of a strong peculiar odour, and a taste at first acrid and acid, but followed by bitterness and astringency. It reddens litmus paper, but afterwards bleaches it. It is insoluble in water, and is prepared by the action of dilute sulphuric or hydrochloric acid on xanthate of potassa. It possesses little permanency, being decomposed by the action of the atmosphere; and at a heat short of 212° it is resolved into bisulphuret of carbon and an inflammable gas.

GENERAL INDEX.

A

Absolute alcohol, 552
Acetates, 503
Acetous fermentation, 579
Acids, definition of, 420
  nomenclature of, 123
  animal, 593
  sulphur, 470
  vegetable, 497
Acid, acetic and acetous, 502
  allantoic, 596
  ambreic, 601
  amniotic, 596
  amylic, 537
  antimonic and antimonious, 377
  arsenic, 357
  arsenious, 354
  aspartic, 570
  auric, 404
  azulmic, 267, 571
  benzoic, 512
  boletic, 520
  boracic, 205
  boro-hydrofluoric, 241
  bromic, 236
  butyric, capric, and caproic, 599
  caffeic, 571
  caincic, 521
  camphoric, 256, 519
  carbazotic, 522
  carbonic, 187
  caseic, 568
  ceric, 548
  chloric, 217
  chloriodic, 231
  chlorocarbonic, 222
  chlorocyanic, 274
  chlorous, 217
  chloroxalic, 520
  cholesteric, 600
  cholic, 620
  chromic, 361
  citric, 508
  columbic, 373
  crameric, 521
  croconic, 501
Acid, crotonic, 599
  cyanic, 270
  cyanilic, 662
  cyano-hydrosulphuric, 277
  cyanuric, 273
  elaiodic, 599
  ellagic, 518
  erythric, 594
  ethero-phosphoric, 558
  ethero-sulphuric, 558
  ferrocyanic, 489
  ferruretted chyazic, 489
  fluoboric, 240
  fluoric, 239
  fluosilicic, 326
  formic, 269, 499, 595
  fulminic, 272
  gallic, 516
  glacial phosphoric, 204
  hippuric, 595
  hircic, 599
  hydriodic, 228
  hydrobromic, 235
  hydrochloric, 212
  hydrocyanic, 266, 520
  hydroferrocyanic, 489
  hydrofluoric, 238
  hydropersulphuric, 261
  hydroselenic, 261
  hydroseleniocyanic, 278
  hydrosulphocyanic, 276
  hydrosulphuric, 258
  hydrotelluric, 387
  hydroxanthic, 664.
  hyponitrous, 178
  hypophosphorous, 201
  hyposulphuric, 197
  hyposulphurous, 196
  igasuric, 520
  indigo-sulphuric, 565
  indigotic, 521
  iodic, 229
  iodous, 229
  jatrophic, 599
  kinic, 506
  lactic, 505
  lactucic, 521

- Acid, lampic, 555
  - lithic, 593
  - malic, 507
  - manganic, 332
  - margaric, 598
  - margaritic, 599
  - mechloic, 575
  - meconic, 513
  - mellitic, 501
  - metagallic, 518
  - metameconic, 514
  - metaphosphoric, 204
  - molybdic and molybdous, 370
  - moric or moroxylic, 519
  - mucic, 518
  - muriatic, 212
  - nanceic, 505
  - nitric, 181
  - nitro-muriatic, 215
  - nitrous, 179
  - oleic, 598
  - osmic, 413
  - oxalic, 498
  - oxy-muriatic, 209
  - oxyprussic, 274
  - paracyanuric, 274
  - paraphosphoric, 202
  - paratartaric, 512
  - pectic, 520
  - perchloric, 218
  - periodic, 230
  - permanganic, 332
  - phocenic, 599
  - phosphatic, 202
  - phosphoric, 202
  - phosphorous, 201
  - prussic, 266, 520
  - purpuric, 594
  - pyrocitric, 509
  - pyrogallic, 517
  - pyrokinic, 507
  - pyroligneous, 502
  - pyromalic, 507
  - pyromucic, 519
  - pyrophosphoric, 203
  - pyrotartaric, 509
  - pyro-uric, 594
  - racemic, 511
  - rheumic, 520
  - ricinic, 599
  - rocellic, 519
  - rosacic, 594
  - saccholactic, 518
  - sebacic, 599
  - selenic, 207
  - selenious, 207
  - silicic, 324
  - silicated fluoric, 327
  - silico-hydrofluoric, 327, 485
  - sorbic, 520
- Acid, stearic, 599
  - suberic, 520
  - succinic, 518
  - sulphocyanic, 276
  - sulphonaphthalic, 254
  - sulphovinic, 557
  - sulphuretted chyazic, 276
  - sulphuric, 194
  - sulphuric, fuming, 194
  - sulphurous, 192
  - tannic, 514
  - tannic, artificial, 516
  - tartaric, 509
  - telluric, 386
  - tellurous, 386
  - titanic, 384
  - tungstic, 372
  - ulmic, 571
  - uric, 593
  - valerianic, 519
  - yellow, 588
  - vanadic, 367
  - of the Vosges, 511
  - xanthic, 664
  - zumic, 520
- Adipocire, 600
- Aëriform bodies, 20
- Affinity, chemical, 124
  - table of, 125
  - single elective, 125
  - double elective, 127
  - disposing, 162
  - by what circumstances modified, 128
  - quiescent and divellent, 127
  - measure of, 133
  - changes that accompany, 127
- Agedoite, 569
- Air, atmospheric, 167
  - alkaline, 242
  - fixed, 187
- Alabaster, 438
- Alembroth, salt of, 478
- Albumen, 588
  - vegetable, 568
  - incipient, 622
- Alcoates, 553
- Alcohol, 552
  - of sulphur, 278
- Algaroth, powder of, 375
- Alizarine, 567
- Alkali, definition of, 420
  - volatile, 242
  - silicated, 325
- Alkalies, vegetable, 523
- Alkaline air, 242
  - bases, 420
  - earths, 292
- Alkalimeter, 463
- Allanite, 381

Alloys, 283, 416
Almond oil, 513
Aloes, bitter of, 523
Althea, 532
Alum, 441
  stone, 441
Alumen ustum, 442
Alumina, or aluminous earth, 307
  sulphates of, 439
  sulphates, double, of, 441
  acetate of, 504
Aluminite, 439
Aluminium and its compounds, 315
  oxyfluoride of, 486
Amalgams, 416
Amalgam *for looking-glasses*, 416
  ammoniacal, 166
  for electrical machines, 416
Amalgamation of silver ores, 400
Amber, 518, 547
Ambergris and ambreine, 601
American hiccory, 567
Amidine, 536
Ammelide, 662
Ammeline, 662
Ammonia, liquid, 243
  character of the salts of, 242
  cobaltate of, 350
  sulphate of, 438
  sulphates, double, of, 442
  sulphite of, 443
  nitrate of, 446
  phosphates of, 453
  arseniates of, 458
  carbonates of, 464
  hydro-salts of, 467
  sulphur-salts of, 470
  haloid salts of, 477
  chlorides with, 489
  oxalate of, 500
  acetate of, 504
  lactate of, 506
  magnesian phosphate of, 454
  subcarbonate of, 465
  bimalate of, 507
  citrate of, 508
  succinate of, 518
Ammoniacal gas, 242
Ammoniaret of copper, 440
Amnios, liquor of, 625
Amygdaline, 573
Analysis defined, 4
  proximate and ultimate, of organic substances, 495
  of minerals, 639
  of gases, 637
  of mineral waters, 644
Anhydrite, 438
Animal chemistry, 587
  proximate substances, 587
Animal substances, analysis of, 494
  oils and fats, 596
  acids, 593
  jelly, 590
  heat, 615
  fluids, 617
  solids, 633
Antimonialis, pulvis, 377
Antimoniates, 377
Antimonites, 377
Antimony and its compounds, 374
  regulus of, 374
  argentine, flowers of, 375
  glass, crocus, and liver of, 378
  alloys of, 417
  golden sulphuret of, 378
  oxychloride of, 481
  tartrate of, and potassa, 510
  test of, 376
Antimonio-sulphurets, 476
Anthracite, 552
Apatite, 453
Aposepedine, 624
Apparatus, Donovan's, 297
  Nooth's, 188
Aqua potassæ, 296
  fortis, 181
  regia, 215
Arbor Dianæ, 401
  Saturni, 393
Archil, 566
Aricina, 530
Arrangement of the work, 4
Arrow-root, 537
Arseniates, 357, 456
Arsenites, 354
Arsenic and its compounds, 353
  white oxide of, 354
  tests of, 355
  alloys of, 416
  fuming liquor of, 357
Arsenio-sulphurets, 474
Arsenical solution, 459
Arseniuretted hydrogen, 358
Arthanatin, 573
Arterialization, 609
Asparagin, 569
Asphaltum, 549
Atmospheric air, 167
  chemical properties of, 170
  physical properties of, 168
  analysis of, 170
  weight of, 167
Atom, definition of, 142
Atomic theory, Dalton's view of, 142
  weights, 143
Attraction, chemical, vide affinity, 124
  cohesive, 2
  terrestrial, or gravity, 2
  electric, 71

Aurates, 404
Auro-chlorides, 478
Azote, 166

B

Baldwin's phosphorus, 69
Balloons, 159
Balsams, 547
Barilla, 464
Barito-calcite, 467
Barium and its compounds, 306
Baryta or barytes, 307
  hydrate of, 307
  tests of, 307
  sulphate of, 438
  nitrate of, 446
  nitrite of, 448
  chlorate of, 448
  arseniates of, 458
  carbonate of, 465
  double carbonates of, 467
  metaphosphate of, 456
Barley, malting, 582
Barometer, correction of, for the effects of heat, 18
Basis in dyeing (mordant), 563
Bassorin, 570
Battley's sedative liquor, 526
Baumé's hydrometer, degrees of, reduced to the common standard, 661
Bell-metal, 417
Benzin, 663
Benzoates, 513
Benzoin, 512
Benzone, 663
Benzule, 513, 543
Benzamide, 545
Benzoine, 545
Berlin or Prussian blue, 490
Berberin, 572
Bile, 619
Biliary concretions, 620
Bismuth and its compounds, 382
  magistery of, 383
  butter of, 383
  alloys of, 417
Bitter almonds, oil of, 543
Bittern, 233
Bituminous substances, 549
  wood, 551
Bitumen, 549
Black dyes, 567
Black flux, 357, 510
Black lead, 340
Black oxide of iron, 336, 337
  oxide of copper, 389
  vomit, 609
Bleaching, 211
Bleaching powder, 313
Blende, 343
Block tin, 345
Blood, 601
  in disease, 607
  cruor or crassamentum of, 602
  coagulation of, 606
  serum of, 604
  serosity, 604
  colouring matter of, 604
  fibrin of, 606
  buffy coat of, 602
Blood-root, 533
Blowpipe with oxygen, 161
  with oxygen and hydrogen, 160
Blue, Prussian or Berlin, 490
  Saxon, 565
Blue dyes, 564
Boa constrictor, urine of, 593
Bodies, isomorphous, 429
  isomeric, 152
  plesiomorphous, 433
Boiling point of liquids, 42
Bone earth, 453
Boracite, 461
Bones, 633
Borates, 460
Borax, 461
  glass of, 461
Boro-fluorides, 484
Boron and its acids, 204
  terchloride of, 223
Boyle, fuming liquor of, 469
Brain, analysis of, 635
Brass, 417
  brazing, 417
Brazil wood, 566
Bromates, 450
Bromides, 237, 286
  double, 484
Bromide of hydrocarbon, 250
  of cyanogen, 276
Bromine, 233
  its compounds, 235
Brown coal, 551
Bronze, 417
Brucia, 531
Brunswick green, 482
Bryonin, 572
Butter, 622
  of zinc, 343
  of bismuth, 383
Butyrine, 599

C

Cadmium and its compounds, 343
Caffein, 570
Calamine, 342
Calcium and its compounds, 310

Calcination, 283
Calculi, urinary, 631
    biliary, 620
    salivary, 617
Calculus, mulberry, 501
    fibrinous, 633
    uric acid, 631
    bone earth, 631
    ammoniaco-magnesian phosphate, 631
    fusible, 632
    cystic oxide, 632
    xanthic 633
Calomel, 396
Caloric, 5
Calorimeter of Lavoisier and Laplace, 31
Calorimotor, 92
Calx, 283
Camphene or camphogen, 255
Camphor, 543
    artificial, 256, 542
Camphorates, 519
Cannel coal, 551
Cannon metal, 417
Canton's phosphorus, 313
Caoutchouc, 547
    volatile liquid of, 548
    mineral, 549
Capacity for heat, 29
Carbon, 184
    chlorides of, 219
    its compounds with oxygen, 187
        with hydrogen, 244
        with nitrogen, 264
        with sulphur, 278
Carbo-sulphurets, 473
Carbonates, general properties of, 461
    double, 467
Carbonic oxide, 189
Carburets, metallic, 292
Carburetted hydrogen, light, 245
Carmine, 566
Cartilage, 633
Caseous matter, 622
    oxide, 623
Cassius, purple of, 346, 405
Cassava, 537
Catechu, 514
Cathartin, 571
Celestine, 438
Cerasin, 538
Cerate, 548
Cerin, 548
Cerium and its compounds, 381
    oxy-chloride of, 481
Cerulin, 565
Ceruse, 466
Cerussa acetata, 504
Cetine, 60
Cetrarin, 572
Chalk, 465
Chameleon, mineral, 332
Charcoal, 185
    animal, or ivory black, 185
Cheese, 622
Chemical affinity or attraction, 124
    symbols, 150
    equivalents, 141
    mode of ascertaining, 139
    scale of, 141
    formulæ, 150
Chemistry, definition of, 3
    analytical, 637
    organic, 493
    inorganic, 121
    vegetable, 495
    animal, 587
Classification of chemical substances, 4
Cleavage, 428
Chlorates, 218
Chloric ether, 248
Chloral, 222
Chlorides or chlorurets, 211
    metallic, 285
Chlorides with ammonia, 482
    with phosphuretted hydrogen, 482
Chlorides of carbon, 219
    hydrocarbon, 248
    sulphur, 221
    phosphorus, 221
    boron, 223
    iodine, 231
    bromine, 237
    cyanogen, 274
    nitrogen, 219
    lime, 313
    soda, 303
Chlorine, 209
    its compounds, 212
    nature of, 224
    bleaching powers of, 211
    disinfecting powers of, 211
    theories of, 224
Chlorophane, 69
Chlorurets, 211
Chlorophyle, 573
Chloro-nitrous gas, 223
Choke-damp, 189
Cholesterine, 600
Chromates, 459
    of chlorides, 460
Chromate of iron, 359
Chromium and its compounds, 359
    sulphate of, 440
    sulphate, double, of, 442
    oxalate of, and potassa, 501
Chrome alums, 442
Chrome yellow, 460
Chyle, 621

Chyme, 618
Cinchona bark, active principle of, 528
Cinchonia, 528
Cinnabar, 399
Cinnabar, factitious, 399
Citrates, 508
Citrene, 256
Coke, 552
Cloves, oil of, 543
Coal, 551
    gas, 256
    mines, fire-damp of, 246
Coagulation of the blood, 606
Cobalt, and its compounds, 348
    sulphate of, 440
Cobaltate of ammonia, 350
Cobalto-cyanuret of potassium, 492
Cocculus Indicus, principle of, 532
Cochineal, 566
Codeia, 527
Cohesive attraction, 2
    influence of, over chemical action, 128
Cold, artificial methods of producing, 39
Colocyntin, 572
Colouring matter of the blood, 604
Colouring matters, 563
Colours, adjective and substantive, 564
Columbin, 575
Columbium and its compounds, 373
Combination defined, 134
    utility of laws of, 138
    laws of, 134
    historical facts relating to laws of, 138
Combinations, metallic, 284
Combining proportions explained, 135
    table of, 141
    exemplifications of, 137
Combustion, 156
    theories of, 156
    spontaneous, *v.* Phosphuretted hydrogen and Pyrophorus
Composition of bodies, 136
    how determined, 139
Condenser, 80
Conductor, prime, 75
Conductors of heat, 7
Conduction of heat, 6
Cooling of bodies, 14
    velocity of, 14
    law of, by Newton, 14
Copal, 546
Copper nickel, 350
Copper and its compounds, 387
    test of, 389
    alloys of, 417
    pyrites, 387
    glance, 390
Copper, sulphates of, 440
    nitrate of, 446
    arsenite of, 459
    carbonate of, 466
    tinning of, 417
    acetates of, 504
    black, 389
    ammoniacal sulphate of, 355, 440
    white muriate of, 389
    sheathing, preservation of, 89
    resin of, 389
    white of the Chinese, 417
    ore, blue, 466
Cork, 571
Corrosive sublimate, 397
    tests of, 398
Corydalia, 532
Corundum, 316
Coumarin, 545
Count Rumford's mode of ascertaining conducting power of articles of clothing, 7
Cream of milk, 622
    of lime, 311
    of tartar, 510
Creosote, 549
Crocus of antimony, 378
Cryolite, 486
Cryophorus, 46
Crystallization, 424
    systems of, 428
    water of, 423
Crystallography, 421
Crystals, primary form of, 425
    secondary form of, 425
    angles, planes, edges of, in, 425
    structure of, 428
    cleavage of, 428
Curcuma paper, 567
Curd, 622
Cuticle, 634
Cyanogen, 264
    compounds of, 266
    chlorides of, 274, 275
    iodide of, 275
    bromide of, 276
    bisulphuret of, 277
    sulphuret of, 277
Cyanurets, metallic, (or cyanides,) 289
    double, 486
Cyanuret, red, of potassium and iron, 490
Cynopia, 532
Cystic oxide calculus, 632
Cytisin, 571

D

Daphnia, 533
Decomposition, simple, 125

Decomposition, double, 126
Decrepitation, 423
Definite proportions, doctrine of, 135
Deflagration, 283, 444
Dephlogisticated air, 153
  marine acid, 209
Deliquescence, 423
Delphia, 532
Derosne, salt of, 526
Derbyshire spar, 312
Destructive distillation, 495
Detonating powders, 448
Dew, formation of, 13
Dew-point, 52
Diabetic urine, 629
Diathermanous substances, 68
Diamond, 186
Differential thermometer, 23
Diffusiveness, 173
Diffusion tube, 173
Digesting flask, 645
Dippel's oil, 597
Disinfecting liquor, 303
Distillation by descent, 342
  destructive, 495
Dobereiner's lamp, 159
Dragon's blood, 546
Dutch gold, 417
Dyes, 564

E

Earths, pure, 292
  siliceous, 324
Earth, alkaline, 292
  aluminous, 317
Ebullition, 42
Efflorescence, 423
  influence of over affinity, 130
Eggs, 589, 624
Egg-shells, 634
Elaine, 541
Elastic gum, 547
Elasticity, its effects on chemical affinity, 104
  of vapours, 47
Elaterium, 575
Elatin, 575
Elective affinity, 125
  attraction, 71
  repulsion, 71
  excitement, causes of, 75
  intensity, 33
Electricity, 71
  elementary facts of, 71
  conductors and non-conductors, of, 71
  vitreous or positive, 72
  resinous or negative, 72
  theories of, 73
  induction of, 78
Electricity, atmospheric, 77
  identical with lightning, 87
  thermo, 75
  historical notice relating to, 86
  condenser of, 80
Electrical battery, 79
  accumulation, laws of, 83
  machine, 75
  unit jar, 82
Electro-chemical decomposition, theory of, 106
  equivalents, 105
Electro-dynamics, 116
Electro-magnetism, 116
Electrometer, balance, 82
  gold leaf, 80
  torsion, 81
  volta, 106
Electro-negative and positive elements, 107
Electrophorus, 80
Electroscopes and electrometers, 80
Elements, what, and how many, 4
Elementary substances, chemical equivalents of, 141
Emetia, 531
Emetic tartar, 510
Empyreal air, 153
Emulsion, 541
Endosmose, 613
Epsom salt, 438
Equivalents, chemical, 141
  scale of, 141
Erythrogen, 621
Erythronium, 364
Essential oils, 541
  salt of lemons, 500
Ethal, 600
Ether, 554
  theory of the formation of, 556
  acetic, 561
  oxalic, 560
  chloric, 561
  cyanuric, 561
  hydriodic, 560
  hydrochloric, 559
  nitrous, 560
  oxidized, 562
  hydrobromic, 560
  pyroacetic, 562
  sulphocyanic, 561
  sulphuric, 555, 559
  thialic, 661
Etherine, 250
  sulphate of, 559
Ethule or Ethyle, 556
Ethiops mineral, 399
  per se, 395
Euchlorine, 216
Eudiometer, origin of, 171
  Hope's, 638

Eudiometer, Volta's, 637
Eupione, 252
Evaporation, 45
  circumstances influencing, 45
  cause of, 41, 47
  limit to, 49
  Leslie's method of freezing by, 46
Exosmose, 613
Expansion of solids, 16
  of liquids, 18
  of gases, 20
Extractive matter, 573
Extractum Saturni, 504
Eye, humours of, 625
  action of, on light, 62

F

Fat of animals, 596
Feathers, 634
Fecula, 536
Fermentation, 576
  acetous, 579
  panary, 579
  putrefactive, 580
  vinous, 577
  saccharine, 576
Ferro-cyanurets, 486
Ferro-sesquicyanurets, 489
Fibre, woody, 539
Fibrin, 587
  of the blood, 606
Filter, 643
Fire-damp of coal mines, 246
Fixed air, 187
Fixed oils, 540
Flame, *vide* Combustion and Carburetted Hydrogen
Flesh, 634
Flint, 324
Flowers of sulphur, 191
  argentine, of antimony, 375
Fluidity caused by heat, 37
  heat of, 37
Fluoborates of ammonia, 469
Fluosilicate of ammonia, 470
Fluorides, metallic, 287
Fluorides, double, 484
Fluorine, 238
  theories relating to, 239
Fluor spar, 312
Flux, white and black, 510
Fly powder, 353
Food of plants, 585
Form, charges of, exciter of electricity, 77
Freezing mixtures, 39
  tables of, 39
  in vacuo, Leslie's method of, 46
Frigorific mixtures with snow, table of, 39
Friction, heat produced by, 54
  electricity excited by, 75
Fulminating gold, 404
  mercury, 272
  platinum, 409
  silver, 402
Fuming liquor of Libavius, 347
  of Boyle, 469
  of arsenic, 357
Fungin, 571
Funnel, 643
Fusion, 36
  watery, 423
  point of, 282
Fusible metal, 417
Fustic, 567

G

Galena, 391, 394
Gallates, 517
Gall-nuts, 514
Gall-stones, 621
Galvanic battery, 92
  arrangements, 88
Galvanism, 87
  how developed, 87
  effects of, 99
  chemical agency of, 101
  electrical agency of, 100
  connection of, with magnetism, 109
  theories of its production, 94
Galvanometer, 110
Gases, 53
  mode of finding the specific gravity of, 122
  condensation of, 53
  law of expansion of, 21
  diffusion of, 172
  formula for correcting the effects of heat, 49
  specific heat of, 31
  their bulk influenced by moisture, and the formula for correcting its effects, 50
  analysis of mixed, 637
  absorption of, by charcoal, 185
Gases, mode of drying, 53
  coal and oil, 256
  absorption of, by water, 163
Gastric juice, 618
Gelatin, 590
Gentianin, 572
Germination, 581
Gibbsite, 318
Gilding, 416
Glance, silver, 402
  coal, 562

- Glance, copper, 390
- Glass, various kinds of, 325
  - expansion of, by heat, 17
  - of antimony, 378
  - of borax, 461
- Glanber's salt, 437
- Gliadine, 569
- Glucina, 319
  - test of, 320
- Glucinium and its oxide, 319
- Glue, 590
- Gluten, 568
- Glycerine, 599
- Gold and its compounds, 402
  - fulminating compound of, 404
  - ethereal solution of, 405
  - alloys of, 418
  - mosaic, 347
  - haloid salts of, 478
- Golden sulphuret of antimony, 378
- Gong, Chinese, 417
- Goulard's extract, 504
- Gouty concretions, 594
- Grain tin, 345
- Graphite, 340
- Gravel, urinary, 631
- Gravitation, 2
- Gravity, effect of, on chemical action, 133
  - modes of determining specific, 121
- Green, Scheele's, 459
  - mineral, 466
  - Brunswick, 482
- Growth of plants, 583
- Gum, 537
  - resins, 547
  - elastic, 547
  - British, 537
- Gums, 538
- Gunpowder, 445
- Gypsum, 438

H

- Haarkies, 352
- Hair, 634
- Haloid salts, 477
- Hartshorn, spirit of, 242
- Harrowgate water, 649
- Heat, 5
  - definition of, 5
  - nature of, 5
  - communication of, by contact, 6
  - conduction of, 6
  - conductors of, table of, 7
  - radiation of, 8
  - what surfaces best suited for radiation of, 9
  - latent, 30
- Heat, free, 30
  - luminous, 67
  - non-luminous, 11
  - effects of, 15
  - expansion by, 15
    - in solids, 16
    - in liquids, 18
    - in gases, 20
  - exception to the law of, 20
  - how conducted by liquids and gases, 8
  - specific, 29
  - laws of distribution by radiation, 9
  - capacities of bodies for, 29
  - of fluidity, 37
  - sensible and insensible, 30
  - sources of, 54
  - animal, 615
  - radiated, 9
  - reflection of, 10
  - absorption of, 10
  - transmission of, 11
  - theory of, by Prevost and Pictet, 12
  - application of Prevost's theory to the formation of dew, by Dr. Wells, 13
- Heavy spar, 438
- Hematin, 566
- Hæmatite, brown and red, 337
- Hematosine, 604
- Hepar sulphuris, 300
- Hiccory, wild American, 567
- Hogslard, 597
- Hircine, 599
- Homberg's pyrophorus, 442
- Honey, 535
- Honey-stone, 501
- Hoofs, 634
- Hordein, 583
- Horn, 634
  - silver, 402
  - quicksilver, 397
  - lead, 394
- Humours of the eye, 625
- Hydrargo-chlorides, 478
- Hydrates, nature of, 163
- Hydro, how employed, 163
- Hydriodates, 228
- Hydro-carbon of the blood, 612
- Hydrocarburet, 245
  - of chlorine, 248
  - of iodine, 249
  - of bromine, 250
- Hydrochlorates, 467
- Hydrogurets, or hydurets, 292
- Hydrocyanates, 267
- Hydrogen, 158
  - properties of, 159

Hydrogen, oxidation of, 159
  peroxide of, 163
  arseniuretted, 358
  bicarburet of, 251
  light carburetted, 245
  and carbon, compounds of, 244
  and carbon, new compounds of, 244
  phosphuretted, 262
  phosphuretted, chlorides with, 482
  perphosphuretted, 263
  and nitrogen, 242
  and potassium, 299
  seleniuretted, 261
  sulphuretted, 258
  persulphuret of, 260
  telluretted, 387
  with metals, 292
  auro-chloride of, 479
  platino-biniodide of, 483
  ferro-cyanuret of, 489
  ferro-sesquicyanuret of, 490
  zinco-cyanuret of, 492
Hydrometer, Baumé's, degrees of, reduced to the common standard, 661
Hydro-salts, 467
Hydro-sulphurets, 471
Hydro-sulphocyanurets, 472
Hygrometers, 51
Hyperoxymuriates, 218

I

Iceland spar, 465
Ice, 19
Idrialine, 255
Igasurates, 520
Imponderables, 9
  influence of over chemical action, 133
Incandescence, 68
Incipient albumen, 622
Indigo, 564
Indigogene, 522, 566
Induction, electric, 78
  Volta-electric, 117
  magneto-electric, 117
Ink, 515
  marking, 447
  sympathetic, 350
Inflammable air of marshes, 245
Ingenhouz's method of ascertaining the conducting power of solids, 7
Insolubility, influence of, on affinity, 130
Insulators, electrical, 72
Inulin, 571
Iodates, 230, 449
Iodide of hydrocarbon, 249
  of cyanogen, 275
Iodides, or iodurets, 231
  metallic, 286
  double, 483
  oxy-, 484
Iodine, 226
  test for, 227
  compounds of, 359
  oxide of, 229
  chlorides of, 231
Ipecacuanha, emetic principle of, 531
Iridium and its compounds, 413
Iridio-chlorides, 481
Iron and its compounds, 334
  ores of, 334
  cast, 335
  rusting of, 335
  pyrites, 339
  pyrites, magnetic, 340
  sulphates of, 439
  alum, 442
  meteoric, components of, 334
  chromate of, 459
  carbonate of, 466
  ferro-sesquicyanuret of, 490
Isinglass, 590
Isomeric bodies, 152
Isomorphism, 429
Isomorphous substances, table of, 430
Ivory black, 185

J

Jelly, animal, 590
  vegetable, 538
Jet, 551

K

Kali, 296
Kalium, 294
Kermes mineral, 378
Kelp, 464
Kinates, 507
King's yellow, 359
Kupfer-nickel, 350

L

Labarraque's soda liquid, 303
Lac sulphuris, 192
Lakes, 563
Lactates, 506
Lamp without flame, 555
  safety, 246
Lampblack, 546
Lapis causticus, 296

- Lapis infernalis, 447
  - lazuli, 303
- Lard, 597
- Latent heat, 30
- Lateritious sediment, 594
- Law of multiples of combining weights, 137
  - of multiples of combining volumes, 145
- Laws of combination, 134
  - of the distribution of radiant heat, 9
- Lead and its compounds, 391
  - white, 393, 466
  - horn, 394
  - ceruse of, 466
  - nitrates of, 447
  - nitrites of, 448
  - phosphate of, 454
  - arseniates of, 458
  - carbonate of, 466
  - oxychlorides of, 482
  - oxy-iodides of, 484
  - oxy-fluoride of, 486
  - acetates of, 504
  - malate of, 507
  - alloys of, 417
- Lemons, acid of, 508
  - essential salt of, 500
- Lenses, 59 *et seq.*
  - of the eye, 61
- Lepidolite, 305
- Leucine, 588
- Leyden jar, 78
- Libavius, fuming liquor of, 347
- Ligaments, 634
- Light, theories of, 54
  - diffusion of, 55
  - ordinary ray of, 64
  - extraordinary ray of, 64
  - reflection of, 55
  - refraction of, 58
  - refraction, double, of, 64
  - polarized, 64
  - decomposition of, 65
  - calorific rays of, 66
  - prismatic colours of, 65
  - chemical rays of, 67
  - magnetizing rays of, 67
  - necessary to vegetation, 584
  - terrestrial, 68
  - sources of, 68
- Lightning, 87
- Lignin, 539
- Lime, or quicklime, 311
  - water, milk, and hydrate of, 311
  - slaked, 311
  - chloride of, 313
  - sulphate of, 438
  - sulphite of, 443
- Lime, nitrate of, 446
  - phosphates of, 453
  - arseniates of, 458
  - carbonate of, 465
  - double carbonates of, 467
  - oxalate of, 501
  - acetate of, 504
  - stone, 465
- Liniment, volatile, 541
- Liquefaction, 36
- Liquids, expansion of, by heat, 18
  - conducting power of, 8
- Liquor sanguinis, 602
  - silicum, 325
- Liquorice root, sugar of, 535
- Litharge, 392
- Lithia, or lithion, 305
  - sulphate of, 438
  - tests of, 306
- Lithates, 593
- Lithium and its compounds, 305
  - hydro-sulphuret of, 472
  - carbo-sulphuret of, 473
  - arsenio-persulphurets of, 475
  - molybdo-sulphuret of, 476
  - hydrargo-chloride of, 478
- Litmus, 566
  - paper, 644
- Liver of antimony, 378
  - of sulphur, 288, 300
- Logwood, 566
- Luna cornea, 402
- Lunar caustic, 401, 447
- Lupulin, 571
- Lymph, 625

M

- Madder, 567
- Magnesia, 314
  - tests of, 315
  - sulphate of, 438
  - nitrate of, 446
  - phosphates of, 454
  - carbonate of, 465
  - oxalate of, 501
- Magnesian limestone, 467, 640
- Magnesite, 465
- Magnesium and its compounds, 314
  - hydro-sulphuret of, 472
  - arsenio-persulphuret of, 476
- Magnetic iron pyrites, 340
- Magnetism, electro-, 116
- Magneto-electric induction, 117
- Malachite, 466
- Malates, 507
- Maltha, 549
- Malting, 582
- Manganesium, or manganium, 327
- Manganese and its compounds, 327

Manganese, sulphate of, 439
  alum, 492
Manna and mannite, 535
Marble, 465
Massicot, 392
Margarine, 541, 598
Matter, physical properties of, 1
  chemical properties of, 3
  influence of quantity of, over affinity, 132
Meconates, 514
Medullin, 571
Melam, 662
Melamine, 662
Mellon, 662
Membranes, 634
  permeability of, to gases, 613
Mercaptan, 661
Mercaptum, 661
Mercury and its compounds, 395
  with metals, 416
  fulminating compound of, 272
  sulphates of, 440
  nitrates of, 447
  carbonate of, 466
  oxychloride of, 482
  acetate of, 505
Metallic combinations, 414
  bases of the alkalies, 294
  bases of the alkaline earths, 306
  bases of the earths, 315
Metals, 279
  general properties of, 279
  alloys of, 283, 414
  alkaline or alkaligenous, 292
  table of discovery of, 280
  table of specific gravity of, 281
  malleability of, 281
  ductility of, 281
  crystallization of, 282
  tenacity of, 281
  hardness of, 282
  structure of, 282
  native state of, 283
  action of heat on, 283
  action of electricity on, 284
  fusibility of, table of, 282
  oxidation of, 283
  reduction of, 284
  compounds of, with
    chlorine, 285
    iodine, 286
    bromine, 286
    fluorine, 287
    sulphur, 287
    selenium, 289
    cyanogen, 289
    phosphorus, 291
    carbon, 292
    hydrogen, 292
Metals, classification of, 292
Metaphosphates, 456
Meteoric stones, 334
Milk, 622
  sugar of, 592,
Mindererus, spirit of, 504
Mineral chameleon, 332
  green, 466
  yellow, 482
  tar, 549
  pitch, 549
Minerals, analysis of, 639
Mineral waters, analysis of, 644
Minium, 393
Molasses, 535
Molybdates, 370
Molybdenum and its compounds, 368
Molybdo-sulphurets, 476
Mordant, 563
Morphia, 524
  salts of, 526
Mosaic gold, 347
Mother of pearl, 634
Mucilage, 537
Mucus, 625
Mulberry calculus, 501
Multiples, law of, 137, 145
Muriates, 467
Muriatic acid, table of specific gravity of, 214
Muscle, 634
  converted into fat, 600
Mustard, oil of, 543
Mushrooms, peculiar substance of, 571
Myrica cerifera, 548
Myricin, 548

N

Nails of animals, 634
Naphtha, 252
  from coal tar, 253
Naphthaline, 253
  chloride of, 254
Narcotina, 526
Narceia, 528
Natrium, 301
Natron, 302
Neutral salts, characters of, 419
Neutralization, 136
Nickel and its compounds, 350
  alloys of, 417
  sulphate of, 440
Nicotina, 533
Nitrates, 444
Nitrites, 448
Nitre, 445
Nitric oxide gas, 176
Nitrogen gas, 166
  properties of, 166

Nitrogen, oxides of, 167
    protoxide of, 174
    binoxide of, 176
    quadrochloride, 219
    compounds of, with carbon, 264
Nooth's apparatus, 188
Nomenclature, 122

O

Oil, Dippel's animal, 597
    of vitriol, 194
    of wine, 559
    gas, 256
Oils, animal, 596
    fixed, 540
    drying, or siccative, 540
    volatile, or essential, 541
    vegetable, 539
Ointments, 546
Olefiant gas, 247
Oleine, 541, 598
Olive oil, 540
Olivile, 572
Opium, active principle of, 524
    tests of, 526
Organic chemistry, 493
    substances, character of, 495
Orpiment, 359
Osmazome, 634
Osmium and its compounds, 411
Osmio-chlorides, 481
Oxalates, 500
Oxamide, or oxalammide, 500
Oxidation, 154
Oxide, cystic, 632
    xanthic, 633
    caseous, 623
    carbonic, 189
Oxides, what, 123, 284
    nomenclature of, 123
Oxidum manganoso-manganicum, 331
Oxidum ferroso-ferricum, 337
Oxygen, 153
    preparation of, 153
    properties of, 154
    necessary to respiration, 155
Oxyhydrogen blowpipe, 160
Oxymuriate of lime, 313
Oxiodine, 230
Oxychlorides, 481

P

Palladium and its compounds, 409
Palladio-chlorides, 480
Panary fermentation, 579
Pancreatic juice, 618
Paper, test, preparation of, 644
Papin's digester, 43
Paraffine, 251
Paranaphthaline, 255
Particles, integrant and component, 3
Patent yellow, 482
Pearls, 634
Pearlash, 426
Pectin, 539
Pericardium, liquor of, 625
Perchlorates, 449
Perspiration, fluid of, 627
Petroleum, 549
Petroline, 251
Pewter, 417
Phenecin, 565
Phlogiston, 158
Phocenine, 599
Phosgene gas, 222
Phosphates, 450
Phosphites, 201
Phosphorescence, 69
Phosphoric ether, 555
Phosphorus, 198
    its combinations with oxygen, 200
        with hydrogen, 262
    chlorides of, 221
    nituret of, 663
    sulphuret of, 279
    Canton's, 69, 313
    Baldwin's, 69
Phosphurets, metallic, 291
Phosphuretted hydrogen gas, 262
    salts of, 470
    chlorides with, 482
Photometer, 70
Picamar, 551
Picromel, 619
Picrotoxia, 532
Pinchbeck, 417
Piperin, 571
Pitchblende, 379
Pitch, mineral, 549
Pit-coal, 551
Pittacal, 551
Plants, growth of, 583
    digestion of, 584
    food of, 585
    respiration of, 583
Plaster of Paris, 438
Plasters, 546
Platinum and its compounds, 406
    spongy, 480
    fulminating powder of, 409
    alloy of, with arsenic, 417
Platino-chlorides, 479
Plesiomorphism, 433
Plumbagin, 573
Plumbago, 340
Pollenin, 571

- Polychroite, 567
- Populin, 574
- Potash and pearlash, 462
- Potassa, 296
  - hydrate of, 296
  - aqua, 296
  - fusa, 296
  - tests of, 297
  - sulphates of, 437
  - sulphite of, 443
  - nitrate of, 445
  - nitrite of, 448
  - chlorate, oxymuriate, or hyperoxymuriate of, 448
  - iodates of, 449
  - phosphates of, 453
  - arseniates of, 458
  - arsenite of, 459
  - chromates of, 459
  - carbonates of, 462
  - oxalates of, 500
  - acetate of, 503
  - malate of, 507
  - citrate of, 508
  - tartrates of, 509
  - tartrate of, and soda, 510
  - triple prussiate of, 487
- Potassium and its compounds, 294
  - sulphur-salts of, 470
  - haloid salts of, 456
  - hydro-sulphuret of, 471
  - hydro-sulphocyanuret of, 472
  - carbo-sulphuret of, 473
  - arsenio-persulphurets of, 475
  - molybdo-sulphuret of, 476
- Potato, starch of, 536
- Precipitate, red, 396
- Pressure, influence of, on the bulk of gases, 168
- Prism, 65
- Prismatic, or solar spectrum, 65
- Proof-spirit, 553
- Proportions, definite, 134
  - combining, 136
- Proximate analysis, 495
  - principles, 495
    - of vegetables, 495
    - of animals, 587
- Prussian or Berlin blue, 490
- Prussiates, *vide* Hydrocyanates.
- Prussiate, triple, of potassa, 487
  - of mercury, 265
- Pulvis antimonialis, 377
- Purple powder of Cassius, 346, 405
- Purpurates, 594
- Pus, 626
- Putrefaction, 635
- Putrefactive fermentation, 580
- Pyrites, iron, 339
  - copper, 387
- Pyroacetic ether, 562
- Pyroxylic spirit, 562
- Pyrometer of Daniell, 26
  - Wedgwood's, 27
- Pyrophorus of Homberg, 442
- Pyrophosphates, 455

Q

- Quantity, its influence on affinity, 132
- Quercitron bark, 567
- Quicklime, 311
- Quicksilver, 395
  - horn, 397
- Quills, 634
- Quinia, or quinine, 529

R

- Racemates, 512
- Radiation, 8
- Rays of heat, angles of incidence and reflection of, 10
  - luminous, 11
  - non-luminous, 8
- Rays of light, 55
  - angles of incidence and reflection of, 55
  - angles of refraction of, 58
- Realgar, 358
- Red lead, 393
  - precipitate, 396
  - dyes, 566
  - oxide of manganese, 331
  - oxide of copper, 388
- Reduction of metals, 284
- Rennet, 622
- Resin of copper, 389
- Resins, 546
  - gas from, 258
- Respiration, 609
  - of plants, 584
- Retinasphaltum, 549
- Rhaponticin, 572
- Rhein, 572
- Rhodium and its compounds, 410
- Rhodio-chlorides, 480
- Rhubarbarin, 572
- Rochelle salt, 510
- Rouge, 567

S

- Saccharine fermentation, 576
- Saccharum Saturni, 504
- Safety-lamp, Sir H. Davy's, 246
  - improvement of, by Messrs. Upton and Roberts, 247
- Safflower, 567
- Saffron, 567

Sago and salep, 537
Sal ammoniac, 468
Salicin, 574
Salifiable base, 284
Saliva, 617
Salivary matter, 617
Salt, common, 302
    Seignette or Rochelle, 510
    of sorrel, 500
    microcosmic, 453
    of Derosne, 526
    Glauber's, 437
    of lemons, 500
    rock, bay, fishery, and stoved, 302
    petre, 445
    spirit of, 212
Salts, general remarks on, 419
    nomenclature of, 123, 422
    classification of, 422
    affinity of, for water, 423
    crystallization of, 424
    double and triple, 434
    deliquescent, 423
    watery fusion of, 423
    efflorescence of, 423
    water of crystallization of, 423
    decrepitation of, 423
    plesiomorphism of, 433
    of morphia, 526
    isomorphous, 429
    oxy-, 433
    sulphates, 434
        double, 441
    sulphites, 443
    nitrates, 444
    nitrites, 448
    chlorates, 448
    perchlorates, 449
    iodates, 449
    bromates, 450
    phosphates, 450
    pyrophosphates, 455
    metaphosphates, 456
    arseniates, 456
    arsenites, 459
    chromates, 459
    of chlorides, 460
    borates, 460
    carbonates, 461
        double, 467
    hydro-, 467
    of phosphuretted hydrogen, 470
    sulphur-, 470
    hydro-sulphurets, 471
    hydro-sulphocyanurets, 472
    carbo-sulphurets, 473
    arsenio-sulphurets, 474
    molybdo-sulphurets, 476
    antimonio-sulphurets, 476
Salts, tungsto-sulphurets, 477
    haloid, 477
    hydrargo-chlorides, 478
    auro-chlorides, 478
    platino-chlorides, 479
    palladio-chlorides, 480
    rhodio-chlorides, 480
    iridio-chlorides, 481
    osmio-chlorides, 481
    oxy-chlorides, 481
    chlorides with ammonia, 482
    chlorides with phosphuretted hydrogen, 482
    double iodides, 483
    oxy-iodides, 484
    double bromides, 484
    double fluorides, 484
    boro-fluorides, 484
    silico-fluorides, 485
    titano-fluorides, 486
    oxy-fluorides, 486
    double-cyanurets, 486
    ferro-cyanurets, 486
    ferro-sesquicyanurets, 489
    zinco-cyanurets, 492
    cobalto-cyanurets, 492
    oxalates, 500
    acetates, 503
    lactates, 506
    kinates, 507
    malates, 507
    citrates, 508
    tartrates, 509
    benzoates, 513
    meconates, 514
    racemates, 512
    tannates, 516
    gallates, 517
    succinates, 518
    camphorates, 519
    igasurates, 520
Sanguinaria Canadensis, 533
Saponin, 573
Sarcocoll, 572
Saxon blue, 565
Scale of equivalents, 141
Scheele's green, 355, 459
Sea-water, 646
Secreted animal fluids, 617
Sealing-wax, 546
Scillitin, 573
Sediment of urine, 594, 630
Seignette, salt of, 510
Selenite, 438
Selenium, 206
    oxide of, 207
    bisulphuret of, 279
Seleniuretted hydrogen, 261
Seleniurets, metallic, 289
Seleniuret of phosphorus, 279

- Senegin, 573
- Serosity and serum, 604
- Serous membranes, fluid of, 625
- Serum, 602, 604
- Shells, 634
- Silica or siliceous earth, 324
- Silicates, 325
- Silicated alkali, 325
- Silicium and its compounds, 323
- Silico-fluorides, 485
- Silicon, 323
- Silicum, liquor, 325
- Silk, 634
- Silver and its compounds, 400
  - fulminating compound of, 402
  - glance, 402
  - alloys of, 418
  - amalgamation of, 400
  - sulphate of, 440
  - nitrate of, 447
  - phosphate of, 454
  - dipyrophosphate of, 456
  - arseniate of, 458
  - granulated, 401
  - horn, 402
- Sinapisin, 575
- Skin, 634
- Slaked lime, 311
- Slag formed in the reduction of iron, 334
- Smalt, 348
- Soap, 598
- Soda or natron, 302
  - tests of, 302
  - chloride of, 303
  - sulphates of, 437
  - sulphite, 443
  - nitrate of, 446
  - nitrite of, 448
  - perchlorate of, 449
  - phosphates of, 452
  - pyrophosphates of, 455
  - metaphosphate of, 456
  - arseniates of, 458
  - arsenite of, 459
  - biborate of, 461
  - carbonate of, 464
  - oxalate of, 500
  - acetate of, 503
  - malate of, 507
  - citrate of, 508
  - tartrate of, and potassa, 510
  - tartrate of, 510
- Sodium, or natrium, and its compounds, 301
  - chloride of, 302
  - hydro-sulphuret of, 472
- Solania, 532
- Solar rays, 65
- Solders, 417
- Solids, expansion of by heat, 15
  - liquefaction of, 36
  - conducting power of, 6
  - specific heat of, 29
- Solution, 124
- Sorrel, salt of, 500
- Spar, Iceland, 465
  - fluor, 312
  - heavy, 438
- Specific gravity, 121
  - heat, 29
    - relation of, to the atomic weights, 35
    - of gases, 31
- Speculum metal, 417
- Spectrum, solar, 65
  - calorific rays of the, 66
- Spelter, 342
- Spermaceti, 600
  - oil, 597
- Spirit, proof, 553
  - of wine, 552
  - pyroxylic, 562
  - pyroacetic, 562
  - of Mindererus, 504
  - of hartshorn, 242
- Stannates, 346
- Starch, 536
- Starkey's soap, 542
- Steam, temperature of, 43
  - elasticity of, 44
  - latent heat of, 45
- Steam-engine, principle of, 44
- Stearine, 541, 597
- Steel, 341
  - Indian (wootz,) 418
  - alloys of, 418
- Stream tin, 345
- Stibium, 374
- Strontia, or strontites, 309
  - tests of, 310
  - sulphate of, 438
  - nitrate of, 446
  - nitrite of, 448
  - carbonate of, 465
  - acetate of, 504
- Strontianite, 465
- Strontium and its compounds, 309
  - hydro-sulphuret of, 472
  - carbo-sulphuret of, 473
- Strychnia, 530
- Suberin, 571
- Succinates, 518
- Suet, 597
- Sugar, 534
  - of lead, 504
  - of starch, 537
  - of grapes, 535
  - of liquorice, 535
  - of milk, 592

Sugar of diabetes, 592
Sugar-candy, 534
Sulpho-sinapisin, 575
Sulphates, 434
  double, 441
Sulphites, 443
Sulpho-benzide, 663
Sulphur, 191
  oxides of, 192
  flowers of, 191
  hydrate of, 192
  chlorides of, 221
Sulphuris, lac, 192
Sulphur-acids, 470
Sulphurets, metallic, 287
Sulphuretted hydrogen, 258
Sulphuretted sulphites, 197
Sulphuric ether, 554
Sulphur, balsam of, 542
  salts, 470
  bases, 470
Sun, heat produced by the, 66
Supporters of combustion, 156
Surturbrand, 551
Sweat, 627
Synthesis defined, 4

T

Tallow, 597
Tannic acid, or tannin, 514
  artificial, formation of, 516,
Tanno-gelatin, 515
Tantalum, 373
Tantalite, 373
Tapioca, 537
Tar, inflammable principles of, 549
  mineral, 549
Tartar, 510
  cream of, 510
  soluble, 509
  emetic, 510
Tartrates, 509
Tears, 625
Teeth, 634
Telescope, construction of, 57
Telluretted hydrogen, 387
Tellurium and its compounds, 385
Temperature, what, 28
  equilibrium of, 9
Tenacity of metals, 281
Tendons, 634
Thermometer, or thermoscope, 23
  air, 23
  differential, 23
  formula for converting the expression of one into another, 25
  graduation of, 25
  register, 27
Thorina, 321
  tests of, 321
Thorium and its compounds, 321
Tin and its compounds, 345
  alloys of, 417
  oxychlorides of, 481
  permuriate of, 347
Tincal, 461
Titanium and its compounds, 383
Titano-fluorides, 486
Tombac, 417
Traubensäure, 511
Transfer, galvanic, 101
Train oil, 597
Treacle, 535
Trona, 464
Trough, galvanic, 92
Tungsten and its compounds, 371
Tungstates, 372
Tungsto-sulphurets, 477
Turpeth mineral, 440
Turmeric, 567
  paper, 644
Turnsol, 566
Turpentine, oil of, 542
Turkey red, 567
Type, metal for, 417

U

Ulmin, 571
Ultimate analysis, 495
Ultramarine, 303
Uranium and its compounds, 379
Urates, 593
Urea, 591
Urine, 627
  of the boa constrictor, 593
Urinary concretions or calculi, 631

V

Vacuum, boiling in, 43
  evaporation in, 46
Vanadium and its compounds, 363
Vaporization, 41
  cause of, 41
Vapour, dilatation of, 42
  density of, 41
  elasticity or tension of, 47
  latent heat of, 45
  presence of, in gases, 50
  table of the elastic force of, 44
Varvicite, 331
Vegetable acids, 497
  acids, table of, 497
  alkalies, 523
    table of, 524
    preparation of, 524
  extract, 573

Vegetable jelly, 538
  gluten and albumen, 568
  chemistry, 495
  substances, 494
    having oxygen and hydrogen in the same ratio as in water, 533
    oleaginous, resinous, and bituminous, 539
Vegetation, 583
Veratria, 531
Verdigris, 505
Verditer, 466
Vermilion, 399
Vinegar, 580
Vinous fermentation, 577
Vision, 62
Vital air, 153
Vitriol, oil of, 194
  blue, 440
  green, 439
  white, 439
Volatile alkali, 242
  liniment, 541
Volta-electric induction, 117
  electrometer, 106
Volta's eudiometer, 637
  pile, 92
  theory, 94
Voltaic circles, laws of the action of, 96
Volumes, theory of, 144
  combining, 145
    table of, 146

W

Water, composition of, 161
  properties of, 162
  expansion of, in freezing, 19
  boiling and freezing points of, 25
  of crystallization, 423
  rain, snow, spring, well, and river, 644
  of the sea and the Dead Sea, 646
Waters, mineral, 644
  tables of composition of, 648
  acidulous, 644
  alkaline, 645
Waters, chalybeate and sulphuretted, 645
  siliceous, 647
  saline, 645
Wax, 548
Welding, 334
Wheat-flour, 536
Whey, 622
White lead, 466
  copper, 417
Wine, quantity of alcohol in, 554
  oil of, 559
Wires, tenacity of, table of, 282
Wismuth, 382
Witherite, 465
Wood, bituminous, 551
Woody fibre, 539
Wool, 634
Wootz, 418

X

Xanthic oxide calculus, 633

Y

Yeast, 569
Yellow, mineral or patent, 482
  King's, 359
  chrome, 460
  dyes, 567
Yttria and its base, 320

Z

Zanthopicrin, 572
Zaffre, 348
Zymome, 569
Zinc and its compounds, 341
  blende, 343
  brown and blue blaze of, 342
  butter of, 343
  alloys of, 417
  amalgam of, 416
  sulphate of, 439
  acetate of, 505
Zinco-cyanurets, 492
Zincum, 341
Zirconium and its compounds, 322

ERRATA.

Page 107, in the list of negative electrics, insert *bromine* between chlorine and iodine.
107, in the list of positive electrics, insert *thorium* between zirconium and manganese.
141, equivalent of tellurium, for 32.3 read 64.2, being the number given at page 385 as more correct.
212, in the formula for chloral, for 9Cl read 9C
363, line 43, for *Jaberg* read *Taberg*.

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